AgNPs Embedded Screen Printed Electrodes Modified with Schiff Base Ionophore for Al(III) Determination

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Submitted by

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Certificate

This is certify that the thesis entitled **“AgNPs Embedded Screen Printed Electrodes Modified with Schiff Base Ionophore for Al(III) Determination”** being submitted by **Mr. Arjun Nain** in partial fulfilment of the requirement for the award of degree of Masters in Chemistry in the School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, is a bonafide work carried out under the supervision of Senior Professor Susheel Mittal and that no part of this project has been submitted for the award of any other degree.

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Candidate's Declaration

I hereby declare that the work being presented in the thesis entitled "**AgNPs Embedded Screen Printed Electrodes Modified with Schiff Base Ionophore for Al(III) Determination**" in the partial fulfilment of the requirements for the award of the degree of Masters in Chemistry, School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, is my own work during the period of January 2018 to June 2018, under the supervision of Senior Professor Susheel Mittal. I have not submitted the matter embodied in the thesis for the award of my other degree.

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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Acknowledgment

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I am proud to be the son of such good parents whose everlasting desire, patience, belief and funds keep my dreams alive.

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SPEs	Screen printed electrodes
AgNPs	Silver nanoparticles

Abstract

Disposable screen printed electrodes modified with silver nanoparticles (AgNPs) and Schiff base (JS-1, JS-2, and JS-3) were developed and their electrochemical properties were studied using voltammetric techniques. The optimization of supporting electrolyte and scan rate were studied for these compounds. This sensor worked in optimized conditions with KCl (0.1 M) as supporting electrolyte. Schiff base JS-1 has been explored as voltammetric sensor for the sensitive and selective determination of Al(III) ions with in-situ applications. This voltammetric sensor has detection limit of 0.82 µM. It shows good selectivity for Al(III) over a wide variety of alkali, alkaline earth and heavy metal ions. The proposed voltammetric sensor was successfully applied for determination of Al(III) ions in real life samples.

Chapter 1 Introduction

Electrochemistry is growing in importance as specialized sensors are being applied to the detection of chemical, medical, environmental and hazardous materials. These sensors are rapid, highly specific, low cost and can be automated for easy use.[1] Majority of these sensors are built on the principles of voltammetry. Voltammetric techniques involve the application of a potential (E) to a polarized electrode in an electrochemical cell and the resulting current is monitored. The variation of current with applied potential with change in time (t) is monitored. Thus, all the voltammetric techniques are a function of potential, current, and time.[2] These are considered as active techniques (potentiometry is a passive technique) because the concentration of the analyte species changes due to the redox processes occurring on the working electrode.[3] Voltammetry generally uses the three electrodes which are classified as:

Working electrode

The electrochemical event of interest is carried out on the working electrode. The applied potential on the working electrode is controlled using a potentiostat. The working electrode is composed of inert/redox material which lies in range of interest.[4] To promote surface adsorption and provide different potential range, the surface of working electrode can be varied. The maintenance and cleanliness of working electrode is very important as all electrochemical processes occur on the working electrode.[5]

Reference electrode

A reference electrode has a stable and well-defined and stable potential. It stands as a reference point against which the potential of other electrodes is measured in an electrochemical cell. Hence, the reported applied potential is “vs” a specific reference electrode. Saturated calomel electrode (SCE) and the AgCl/Ag electrode are the commonly used reference electrodes. These reference electrodes are generally separated from the solution by a porous frit.[6] Some reference electrodes have a potential independent of the electrolyte used in the cell.[7]

Counter electrode

When potential is applied to the working electrode such that redox reaction of the analyte occurs, current begin to flow. The main purpose of the counter electrode is to complete the electrical circuit. Current is recorded as electrons flow between the working and counter electrodes. The surface area of counter electrode is greater than working electrode so that the kinetics occurring at working electrode are not disturbed. A platinum wire or disk is commonly used as a counter electrode.[8]

These three electrodes should be properly positioned to get the proper results. The reference electrode should be close to the working electrode. The reference electrode is placed in different compartment to avoid contamination. All the voltammetric techniques are classified on the basis of unique requirements of each process.[9] These are classified as:

Cyclic voltammetry

Cyclic voltammetry is a direct method for measuring the potential of a half-cell reaction when both oxidized and reduced forms of the analyte species are stable during the time required to obtain the current-potential curve at different scan rates.[10] Depending on the analysis, one full cycle, partial cycle or a series of cycles can be performed. Cyclic voltammetry is widely used for the study of redox processes, for understanding reaction intermediates, and for obtaining stability of reaction products.[11]

Normal pulse voltammetry

In normal pulse voltammetry, a series of potential pulses of increasing amplitude are applied and the current is measured near the end of each pulse which allows time for the charging current to decay. Solid electrodes are generally used for this process in unstirred solutions.[12]

Differential pulse voltammetry

In this technique, the potential is applied in a series of pulses. Fixed pulses of small amplitude (10 mV to 100 mV) are superimposed on a base potential which change slowly. Current is measured before and after the application of the pulse and plotted against the base potential for each pulse.[13] This technique due to the large number of pulses used is preffered over other methods.[14]

Square wave voltammetry

This technique uses a combined square wave and staircase potential applied to a stationary electrode to measure the current. It provides high speed, excellent sensitivity, and low background noise currents.[15]

The selection of suitable working electrode is very important in all the above mentioned techniques. Generally, the working electrodes are small flat disks of a conductor that are pressed fit into a rod of an inert material such as Teflon or Kel-F, that has a wire contact embedded. It can be glassy carbon, gold, platinum, carbon paste, tin, mercury etc. It is worth mentioning that all these classical electrodes provide good results but their practical applications like sensing become limited due to their time consuming and bulky nature.[16] The use of new technology for extra portability, better sensitivity, selectivity, a wide range, minimal space and power requirement and cost-effective electrodes is the ultimate target.

The screen printed electrodes meet all those requirements. The three electrodes (working, reference, and counter) are printed on the same surface only.[17] Use of different inks available for manufacturing the electrode system is the reason for the versatile nature of these electrodes in being specific for target metal ions .[18] Other possible modifications include:

- Applying desired functionality for irreversible adsorption.
- Covalent bonding of compounds to electrode surface.
- Using polymer films to coat the electrodes.

Host guest theory

Ionophores like Schiff base and their derivatives act as receptors for specific metal ions based on host guest theory. Schiff base as host provides proper guest space to fit a metal ion. Consequently, shift of peaks or new peaks can be observed in the voltammograms. Shape and size of these metal ions play a significant role for proper fit. When the size of guest is larger than the host, a dome-like structure is formed and complete bonding is not possible. When the size of guest is smaller, then bonds are not stable due to larger size of cavity. This shows the requirement of proper size of host and guest is necessary. The interaction of metal ion and the host ionophore is maximum when they are present in 1:1 in terms of concentrations. Also, a proper orientation must be acquired to fit metal ions in ionophores. Sometimes, size and shape of guest and host is same but direction of approach is not same so the overlap is not effective.

Modifications with nanoparticles

Nanoparticles provide a great platform for enhancement in the properties of the electrodes, especially with the screen printed electrodes. Metal nanoparticles provide good conductivity and possess catalytic properties, to enhance the electron transfer between redox centers in proteins and electrode surfaces, and as catalysts to increase electrochemical reactions by acting as “electronic wires”.[19] Oxide nanoparticleshave good biocompatibility and are used to immobilize biomolecules, while semiconductor nanoparticles are often used as labels or tracers for electrochemical analysis.[20] There are several ways to incorporate the nanoparticles on the electrode surface. The nanoparticles can be synthesized using the known chemical techniques and then drop-coated on the electrode surface. The nanoparticles can be synthesized on the electrode surface itself by applying the right potential with the presence of a specific salt solution.

The real reason behind in-depth study of electrodes and voltammetric processes is that it provides the scope of practical applications.[21] Voltammetry has many applications in research and industrial fields which include:

- Quantitative determination of organic and inorganic compounds in aqueous and nonaqueous solutions
- Determination of electron transfer and reaction mechanisms
- Determination of adsorption processes on surfaces
- Measurement of kinetic rates and constants
- Fundamental studies of oxidation and reduction processes in various media
- Determination of thermodynamic properties of solvated species
- Determination of complexation and coordination values
- Determination of redox potentials.

Detection of heavy metals is one of the main applications of voltammetry. Heavy metals are those metals which possess a specific density of more than 5 g/cm^3 and adversely affect the living organisms and environment. These metals are essential to maintain various biochemical and physiological functions in living organisms when present in very low concentrations, however, they become very harmful when they exceed certain threshold concentrations. Although the long-term adverse effects of heavy metals (lung cancer, bone effects, kidney damage, skin cancer), are known, the exposure to such metals is increasing in many parts of the world.[22] Heavy metals are major environmental pollutants and their toxicity is a problem for ecology, nutrition and the environment. Arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment are commonly found heavy metals in waste water.[23] These metals enter the surroundings by natural means and human activities. Soil erosion, sewage discharge, mining etc. are some common sources of heavy metals.[24] These metals have important biological functions such as homeostasis, transport, compartmentalization and binding to required cell constituents. But these metals become problematic when they bind with protein sites which are not made for them and displace original metals from their natural binding sites causing malfunctioning of cells and ultimately toxicity. Therefore many efforts are being made towards detection of heavy metals to stop and lower the damage.

Several type of techniques like atomic absorption spectrometry (AAS), neutron activation analysis (NAA), atomic fluorescence spectrometry, inductively coupled plasma mass Spectrometry, inductively coupled plasma optical emission spectroscopy (ICP-OES), and inductively coupled plasma optical mass spectrometry are available which can be used for the detection of heavy metal ions.[25,26] These intruments are expensive and require properly trained professionals for smooth usage.[27] In contrast, the voltammetric methods offer simplicity, low cost, rapid results, possibility of in situ applications. So, there is need to design new voltammetric methods which are faster and cheaper for the determination of heavy metal ions.

2.1 Optical methods for heavy metal ions detection

Elshehy et. al., (2014) used an alumino silica optical sensor (ASOS) for the detection and removal of trace Co^{2+}, Cu^{2+} and Cd^{2+} ions in water. It provided up to 97% efficiency in controlled waste management.[28] Inductively coupled plasma atomic absorption spectrometry (ICP-AES) was used by **Sabermahani et. al., (2014)** when they detected Cd^{2+} in environmental samples (food, soil and water) with detection limits of 0.025 ng mL^{-1}.[29]

Ping et. al., (2015) prepared a polythiophene derivative poly- (PTMA) which acted as fluorescence sensor for Co^{2+}, Cu^{2+} and Cd^{2} ions with detection limit of 2.5, 2.0 and 83 nM respectively.[30] Also, water soluble CdTe quantum dots (QDs) were prepared by **Gong et. al., (2016)** using simple one pot method for the detection of silver, mercury and copper ions in water and other drinks with detection limit 0.65, 0.063 and 0.088 ng mL^{-1} respectively.[31] **Terra et. al., (2017)** used optically active electrospum nanofibers in sensors for specific detection of heavy metals using colorimetry and fluorescence. Such nanofibers were obtained by the electro spinning technique and further functionalized with optically active dyes, conjugated polymers, carbon based nanoparticles etc.[32] **Postonikov et. al., (2017)** reported a surface plasmon-polariton based functionalized SERS platform for heavy metal ion detection. Even distribution of plasmon intensity on ordered plasmon structure of diethylenetriaminepentaacetic acid (DTPA) to heavy metals allowed the entrapping of heavy metals with detection limit of 10^{-14}M.[33] **Kumar et. al., (2017)** reported the biosynthetic method for synthesis of gold nanoparticles using cinnamon leaf extract with controllable optical properties. The amalgamation tendency of mercury with gold led to detection of Hg^{2+} ions in aqueous media.[34] **Firdaus et. al., (2018)** developed a benzidine based fluorescent chemosensor to detect Sn^{2+} and Pb^{2+} in DMSO-water (1:9 v/v). The compound was found to be an excellent receptor for Sn^{2+} and Pb^{2+} ions via significant fluorescent enhancement which is due to inhibition of charge transfer process and efficient chelation enhanced fluorescence effect. A detection limit of 0.37 and 0.32 µM was reported for Sn^{2+} and Pb^{2+} respectively.[35] **Zhou et. al., (2018)** reported a novel ratiometric fluorescence sensor based on CdTe quantum dots (QDs) doped hydrogel optical fiber for

Fe^{3+} detection in real time. By ratiometric detection of the fluorescence intensities of the two QDs, quantitative and selective detection of Fe3+ ions is achieved with detection limit of 3.5 µM.[36]

2.2 Schiff base derivatives as receptors

Derivatives of Schiff base acts as good receptors for metal ions. **Xu et. al., (2012)** used 2,2;diphenyl-N,N-bis(2-pyridylmethylene)biphenyl-4,4-diamine, a poor fluorescent derivative of Schiff base shows fluorescence for Fe^{3+},Cu^{2+}, Cd^{2+}, Mn^{2+}, Pb^{2+}, Sn^{2+} and Eu^{2+} in CH_3CN-DMSO (9:1, v/v) with red shifts in emission and increased intensity.[37] **Gupta et. al., (2013)** reported that N,N-[bis(pyridine-2-yl)formylidene]butane-1,4-diamine acts as potentiometric sensor for Cd^{2+} with detection limit of 0.05 µM in pH range of 2.0-8.0.[38] **Huang et. al., (2013)** reported a newly synthesized 1,1'-((1E,1'E)-(pyridine-2,6-diylbis (methylene)) bis(azanylidene))bis(napthen-2-ol) compound having high sensitivity for Al^{3+} in EtOH-H_2O (95:5 v/v) as fluorescent sensor.[39] **Afkhami et. al., (2013)** synthesized a Schiff base for the first time for determination of Cd^{2+}, Cu^{2+} and Hg^{2+} ions in water and foodstuff samples.[40] **Choi et. al., (2014)** reported that (E)-9-(((3-(1H-imidazol-1-yl)propyl)imino)methyl)-2,3,6,7-tetrahydro-1,H,5H-pyrido[3,2,1-ij]quinolin-8-ol gives fluorescence for Zn^{2+} and Al^{3+} in DMF solution having pH 7.4. This compound also showed colorimetry with Fe^{2+} and Fe^{3+} changing color of solution from colorless to orange and colorless to purple respectively.[41] **Reath et. al., (2017)** reported that Schiff base moiety containing crown ether with Co^{2+} shows sensitivity towards alkaline earth and alkali metals. Redox potential (-2V to -1V, DMF under N_2) was 130 mV more positive for alkali metals and 250 mV more positive for alkaline earth metals compared to simple Co-ether complex.[42] **Xhu et. al., (2017)** synthesized a fluorescence probe (E)-1-(((2-benzylthio)ethyl)imino)methyl)nephtalen-2-ol molecule from 2-hydroxy-1-napthaldehyde and 2-benzylthio-ethanamine which due to restriction of C=N and naphthalene ring rotation and blockage of photo induced electron transfer from nitrogen to naphthalene ring, is highly selective to Zn^{2+}. The detection limit was found to be 0.5 µM.[43] **Patra et. al., (2017)** reported that benzildihydrazone (10µM) are colorimetric sensitive for Cu^{2+} at physiological pH range in 1:1 MeOH-H_2O medium with detection limit of 36.6 µM, and the color changed from colorless to reddish yellow.[44]

2.3 Nanoparticles modified screen printed electrodes as sensors

Multiwalled carbon nanotubes and gold nanoparticles were used as modifiers on screen printed electrodes by **Rafiee et. al., (2015)** for the determination of methamphetamine (MA) using cyclic voltammetry with 6 nM as limit of detection.[45] **Orefuwa et. al., (2016)** used gold nanoparticles modified screen printed carbon electrodes to detect As^{3+} in water samples with detection limit of 0.8 nM. Gold nanoparticles were synthesized electrochemically on the electrode surface.[46]

Similarly, **Kanyong et. al., (2016)** used the gold nanoparticles modified screen printed electrodes to detect Pb^{2+} and Cu^{2+} simultaneously using the anodic stripping voltammetry in tap water with detection limit of 2.1 and 1.4 nM at low working potentials.[47] Tin oxide (SnO_2) nanoparticles were used to modify screen printed electrodes by **Lavanya et. al., (2016)** for carbamazepine (CBZ) detection. The nanoparticles were synthesized by simple microwave irradiation method. The sensor provided detection limit of 92 nM.[48]

Yawari et. al., (2017) used gold nanoparticles on screen printed gold electrode and investigated the behavior of (S)-warfarin in human serum, tablets with a detection limit of 1.0 nM using differential pulse voltammetry.[49] Carbon screen printed electrode modified with copper nanoparticles was used by **Shabalina et. al., (2017)** to detect ascorbic acid using linear sweep and cyclic voltammetry with 0.5 µM as detection limit. Copper nanoparticles were synthesized by pulsed laser ablation of a copper.[50] Also, **Khairy et. al., (2017)** used cerium oxide nanoparticles modified screen-printed electrodes (CeO_2-SPEs) for the detection of codeine (COD) and caffeine in human serum with a detection limit of 0.043 µM and 2.4 µM respectively with high selectivity, stability and sensing ability.[51]

Table 2.1: Detection of different metal ions using modified SPEs

S. No.	Electrode surface modifiers	Target metal ions	Voltammetric techniques	Reference
1	Bismuth nanoparticles	Pb^{2+}, Cd^{2+}, Zn^{2+}	SWASV	Tessier et. al., (2007)[52]
2	Gold nanoparticles	Sb^{3+}	SWASV	Dominguez et. al., (2007)[53]

3	Multi-walled carbon nanotubes	Zn^{2+}, Cd^{2+}, Pb^{2+}	DPSV	Fu et. al., (2013)[54]
4	Platinum nanoparticles	As^{3+}	CV	Carter et. al., (2009)[55]
5	Au film	Pb^{2+}, Hg^{2+}	SWASV	Chou et. al., (2010)[56]
6	Crown-ether/Hg film	Pb^{2+}	LSASV	Patil et. al., (2010)[57]
7	Bismuth oxide	Tl^{+}	DPASV	Kokkinos et. al., (2010)[58]
8	Polyamine	Cu^{2+}	SWASV	Giorgi et. al., (2014)[59]
9	Calixarene bulk	Pb^{2+}, Hg^{2+}, Cu^{2+}	DPASV	Adarakatti et. al., (2017)[60]
10	Carbonaceous nanospheres	Pb^{2+}, Hg^{2+}	SWASV	Yang et. al., (2013)[61]

SWASV, square wave anodic stripping voltammetry; DPASV, differential pulse anodic stripping voltammetry; LSASV, linear sweep anodic stripping voltammetry; CV, cyclic voltammetry; LSV, linear sweep voltammetry.

2.4 Research gap

In the literature review, we have found that although there are a lot of methods reported for the detection of heavy metal ions, limited work has been done on the screen printed electrodes modified with an ionophore and silver nanoparticles for heavy metal sensing applications.

2.5 Objectives

The objective of the present work is to study the behavior of screen printed electrodes modified with the Schiff base JS-1 and silver nanoparticles for their potential applications in sensing of heavy metal ions.

Chapter 3 Material and Methods

3.1 Chemicals

Nitrate salts of silver, mercury, cadmium, and lithium were obtained from Alpha Aesar and perchlorate salts of sodium, lead, magnesium, cobalt, zinc, copper, iron and lithium were obtained from Sigma Aldrich. Acetonitrile (ACN), dimethyl sulphoxide (DMSO), tetrahydrofuran (THF) and dimethyl formamide (DMF) were purchased from Merck (India). All the solutions were prepared by using double distilled water.

3.2 Preparation of screen printed electrodes

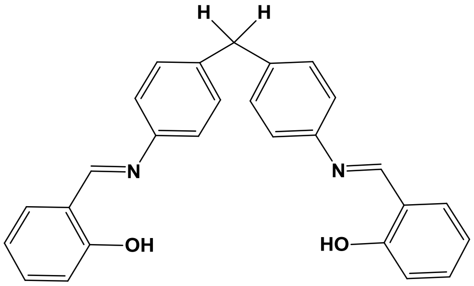
All the experiments carried out in this study used the screen printed electrodes (SPEs) with the dimensions (41 mm×7 mm) composed of three electrodes with 3mm graphite working electrode, a graphite counter and Ag/AgCl reference electrode. These SPEs were fabricated in the laboratory of Professor Craig E. Banks at Manchester Metropolitan University, UK using a microDEK1760RS screen-printing machine (DEK, Weymouth, UK). Firstly, a carbon–graphite ink formulation (product code: C2000802P2; Gwent Electronic Materials Ltd, UK) was printed onto a polyester (Autostat, 250 micron thickness) substrate. This layer was then cured in a fan oven at 60 °C for 30 minutes. Then silver/silver chloride reference electrode was included by screen printing Ag/AgCl paste (product code: C2040308P2; Gwent Electronic Materials Ltd, UK) onto the plastic substrate. Finally, a dielectric paste was then printed onto the polyester substrate to cover the connections.

3.3 Modifications of screen printed electrodes

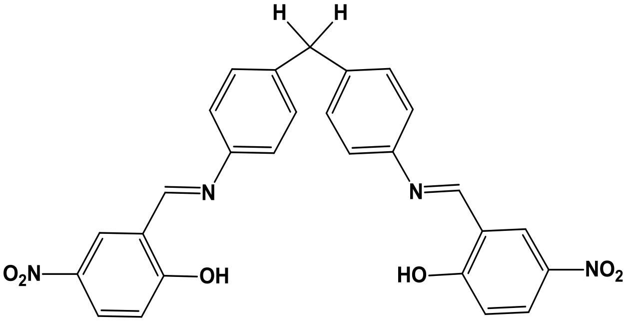
The screen printed electrodes were firstly modified by synthesizing the silver nanoparticles on the working electrode by performing a chronoamperometric scan at -1.2 V using 40 µL of $AgNO_3$ (10^{-4} M) in Britton-Robinson buffer for 100 seconds. Further modification of SPE was carried out by drop-coating ionophore (JS-1) mixed in ACN (10^{-4} M).

3.4 Experimentation

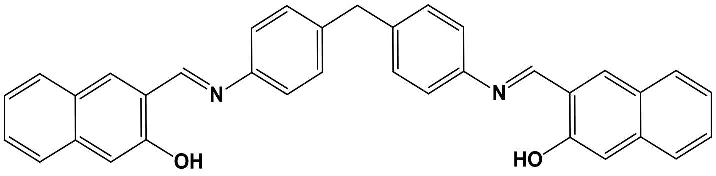
All the experiments were done on the AgNPs and JS-1 modified SPEs using KCl (0.1 M) as supporting electrolyte on the Gamry Potentiostat/Galvanostat/ZRA Interface 1000. After each experiment, the SPE was cleaned using the EDTA solution (0.1 M).



JS-1



JS-2



JS-3

Fig. 3.1: Structures of Ionophores

Chapter 4 Results and Discussions

The host guest theory is commonly used to explain the generation of electrical signals in electroanalytical sensors. The main characteristics of the receptor molecule for behaving as a selective host for the target metal ions are the steric alignment in the molecule and the electronic environment in pseudo cavity. In the present work, it is attempted to check selectivity of the host by varying the electronic environment in the molecule. Since there are two nitrogen and two oxygen atoms present in the cavity, the molecule JS-1 has great potential to act as Lewis base for the transition metal ions. Three variants (JS-1, JS-2 and JS-3) of Schiff base derivatives differs only in the substituents attached to the phenyl ring (Fig. 3.1). Each of the cyclic voltammograms of JS-1, JS-2, and JS-3 were drawn using the AgNPs modified SPE with KCl (0.1 M) as supporting electrolyte (Fig. 4.1).

Cyclic voltammograms of JS-1 and JS-2 show one intense peak in the cathodic region at 0.78 V for JS-1 and 0.69 V for JS-2. Also, a small cathodic peak is obtained at -0.72 V for JS-1 and -0.61 V for JS-2. For JS-3, only one sharp peak at -0.80 V in the cathodic region is observed.

The peaks in the cathodic region observed at -0.72 V and -0.61 V for JS-1 and JS-2 respectively, are observed due to reduction of imine double bond in JS-1 and JS-2, resulting in formation of anion radical, which further gets reduced to full radical and peaks are observed at 0.78 V for JS-1 and 0.69 V for JS-2. Within the molecule, the imine double bond can be reduced with relative ease and so it appears at much lower applied potential of -0.72 V than radical cation which appeared at +0.78 V.

It is interesting to note that due to the presence of nitro group in JS-2, the cyclic voltammogram show slight shift in the cathodic region from JS-1, which shows that the nitro group has little effect on the reduction of imine double bond. Whereas, in case of JS-3, phenyl substituents are present which affect the reduction capability of the imine double bond and as a result, there is only a single cathodic peak at -0.80 V and no other peaks are observed.

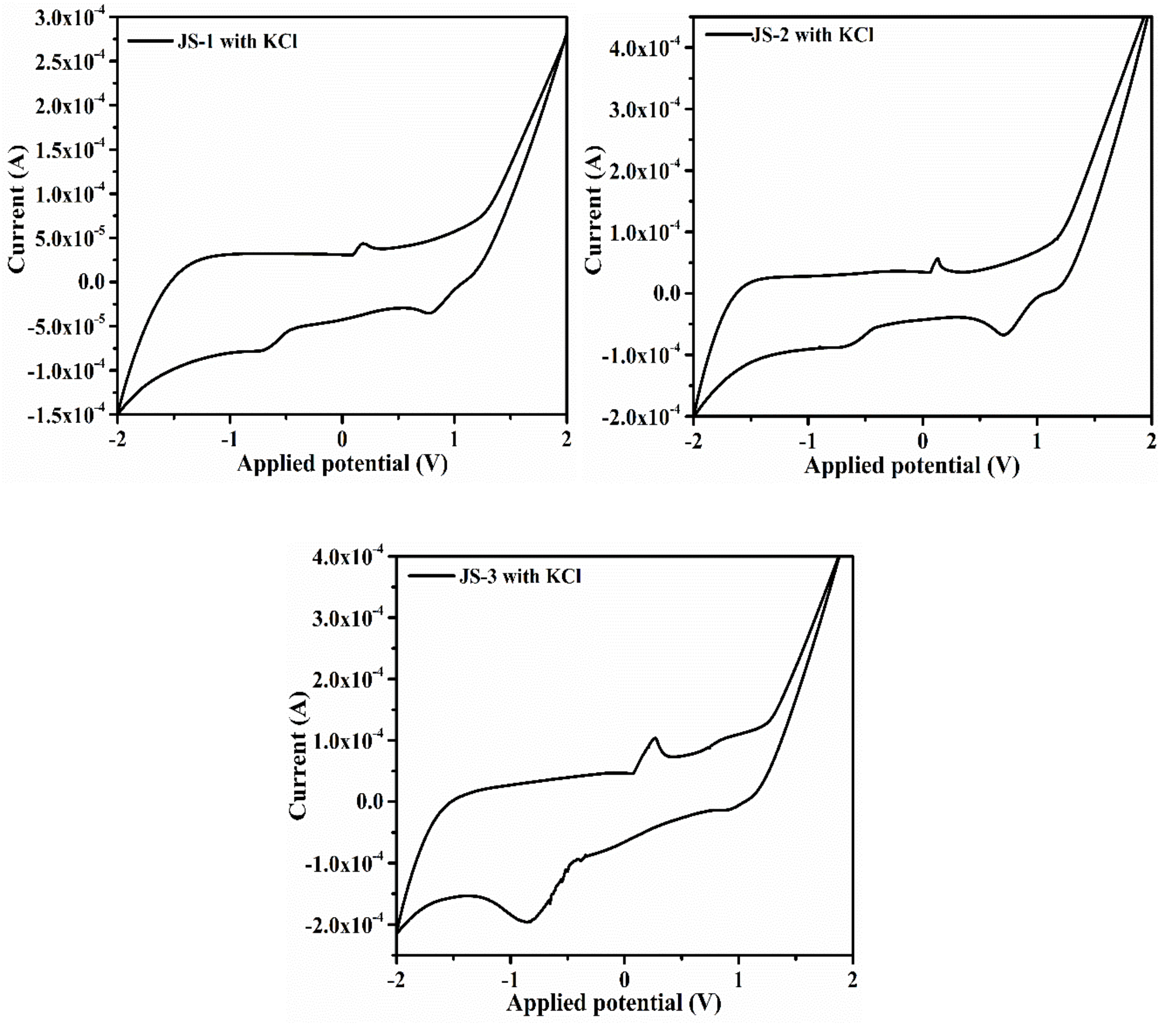


Fig. 4.1: Cyclic voltammograms of JS-1, JS-2 and JS-3 at 20 mV/s on AgNPs modified SPE with KCl (0.1 M) as supporting electrolyte

4.1 Optimization of supporting electrolyte

To study the response of electrolyte on the AgNPs modified SPEs along with ionophores (JS-1, JS-2 and JS-3), different electrolytes (HNO_3 (0.1 M), NaOH (0.1 N), HCl (0.1 M) and KCl (0.1 M)) were used to obtain the cyclic voltammograms which showed that for all the ionophores, well-defined peaks with good current was observed with KCl, while no significant peaks were observed with HCl, NaOH, and HNO_3 (Fig. 4.2, 4.3 and 4.4). Hence, KCl was chosen as the supporting electrolyte for all the voltammetric studies.

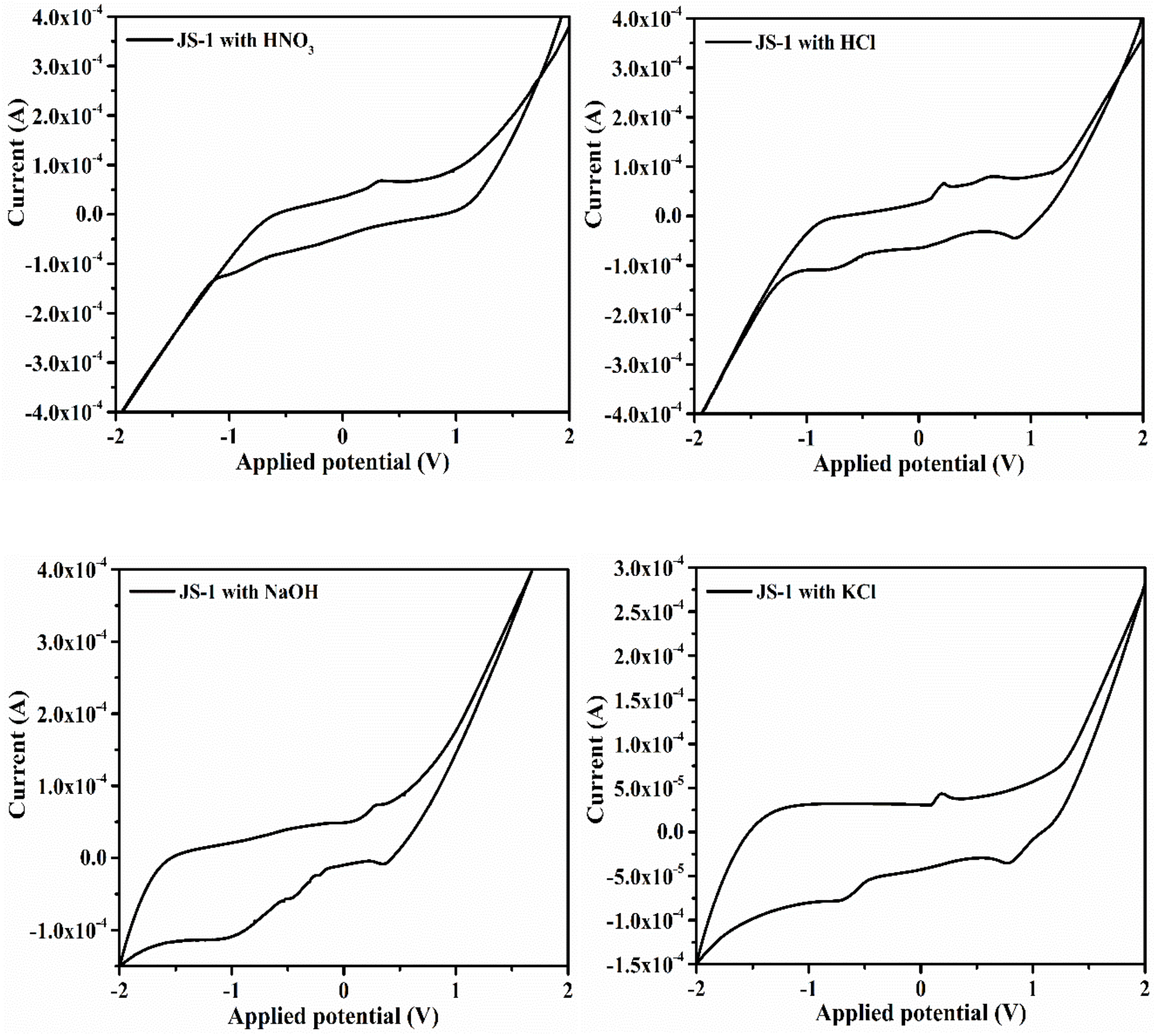


Fig. 4.2: Cyclic voltammograms of JS-1 with different supporting electrolytes (0.1 M) at a scan rate of 20 mV/s on AgNPs modified SPEs

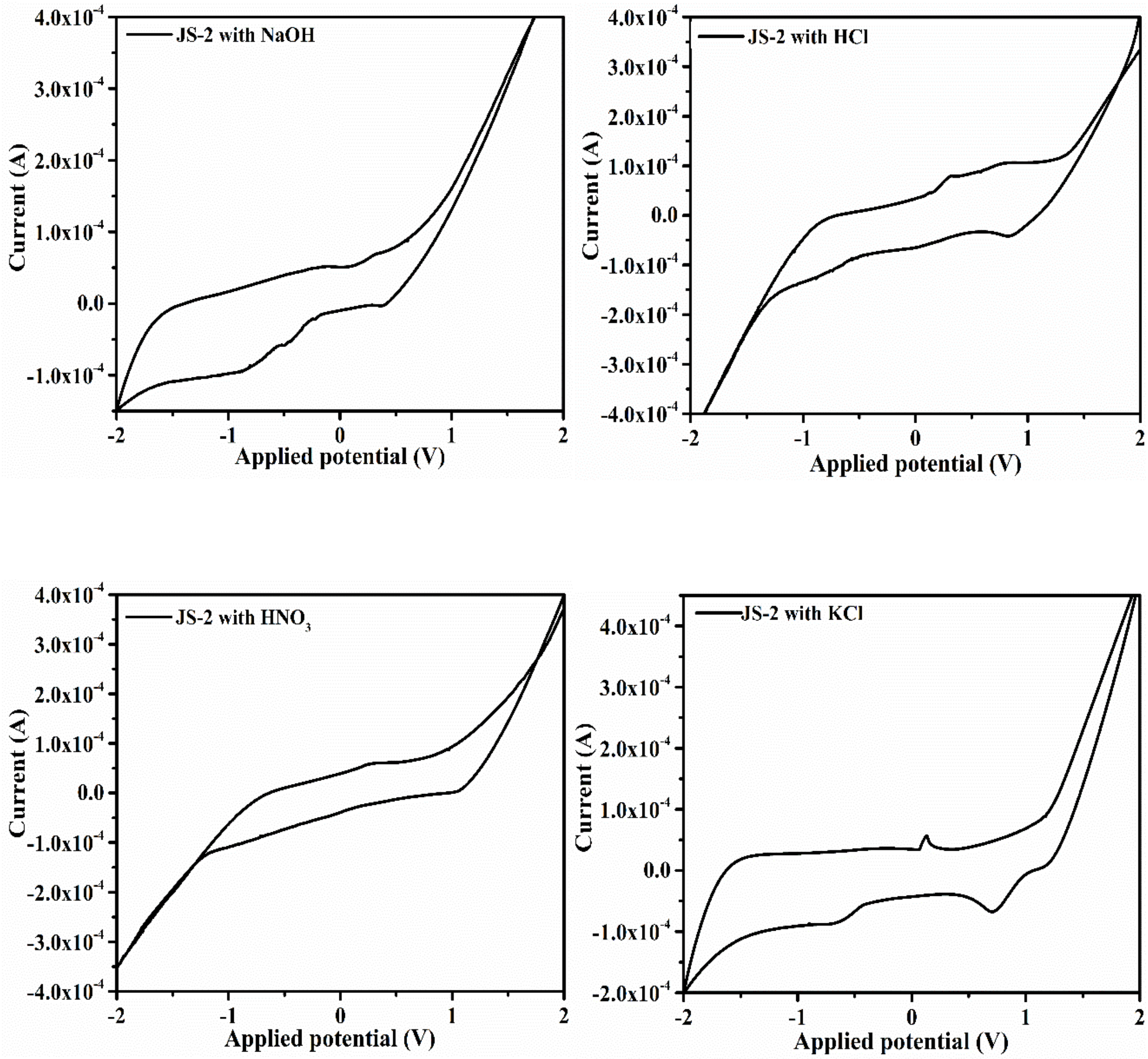


Fig. 4.3: Cyclic voltammograms of JS-2 with different supporting electrolytes (0.1 M) at scan rate of 20 mV/s on AgNPs modified SPEs

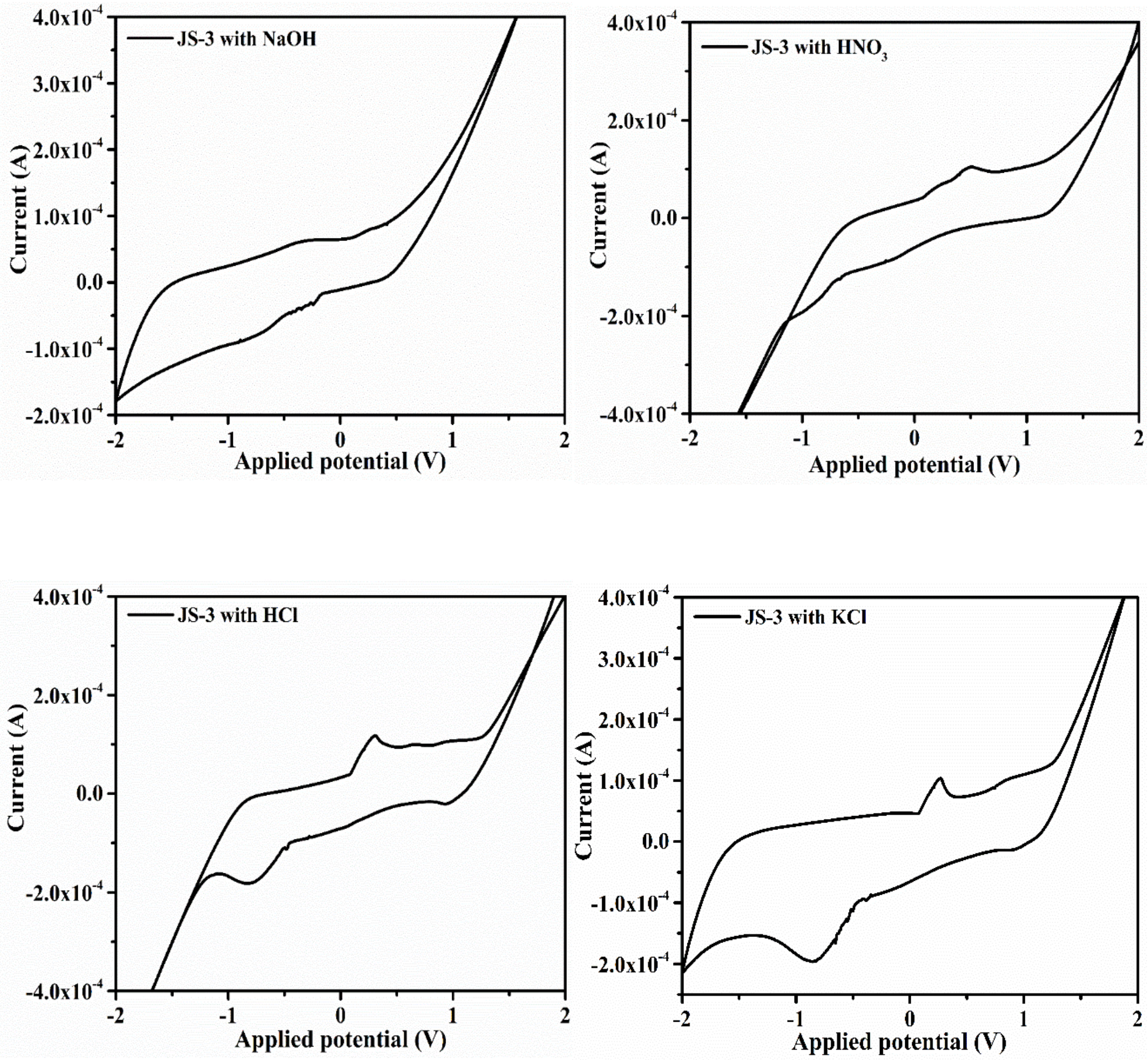


Fig. 4.4: Cyclic voltammograms of JS-3 with different supporting electrolytes (0.1 M) at a scan rate of 20 mV/s on AgNPs modified SPEs

4.2 Effect of Scan Rate

Different scan rates (20 mVs^{-1} to 100mVs^{-1}) were applied on the Schiff base (JS-1, JS-2 and JS-3) modified electrodes to study their kinetic behavior on the electrode surface. Fig. 4.5 shows the effect of scan rate. Peak currents of cathodic waves were plotted against the square root of scan rate as shown in Fig. 4.6. A linear relation in accordance with the Randles-Sevcik equation was obtained between peak current and square root of scan rate. The Randles-Sevcik equation is

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2}$$

where i_p is the peak current, n is the number of electrons involved in the process, A is the surface area of electrode (cm^2), D the diffusion coefficient ($cm^2\ s^{-1}$), C is the concentration of the analyte ($mol\ cm^{-3}$) and ν is scan rate (Vs^{-1}).

Fig. 4.5 shows that with an increase in scan rate, peak current at 0.7 V for JS-1, 0.6 V for JS-2 and 0.57 V for JS-3 increases. This phenomenon shows that diffusion controlled process was observed on the three above mentioned electrodes.

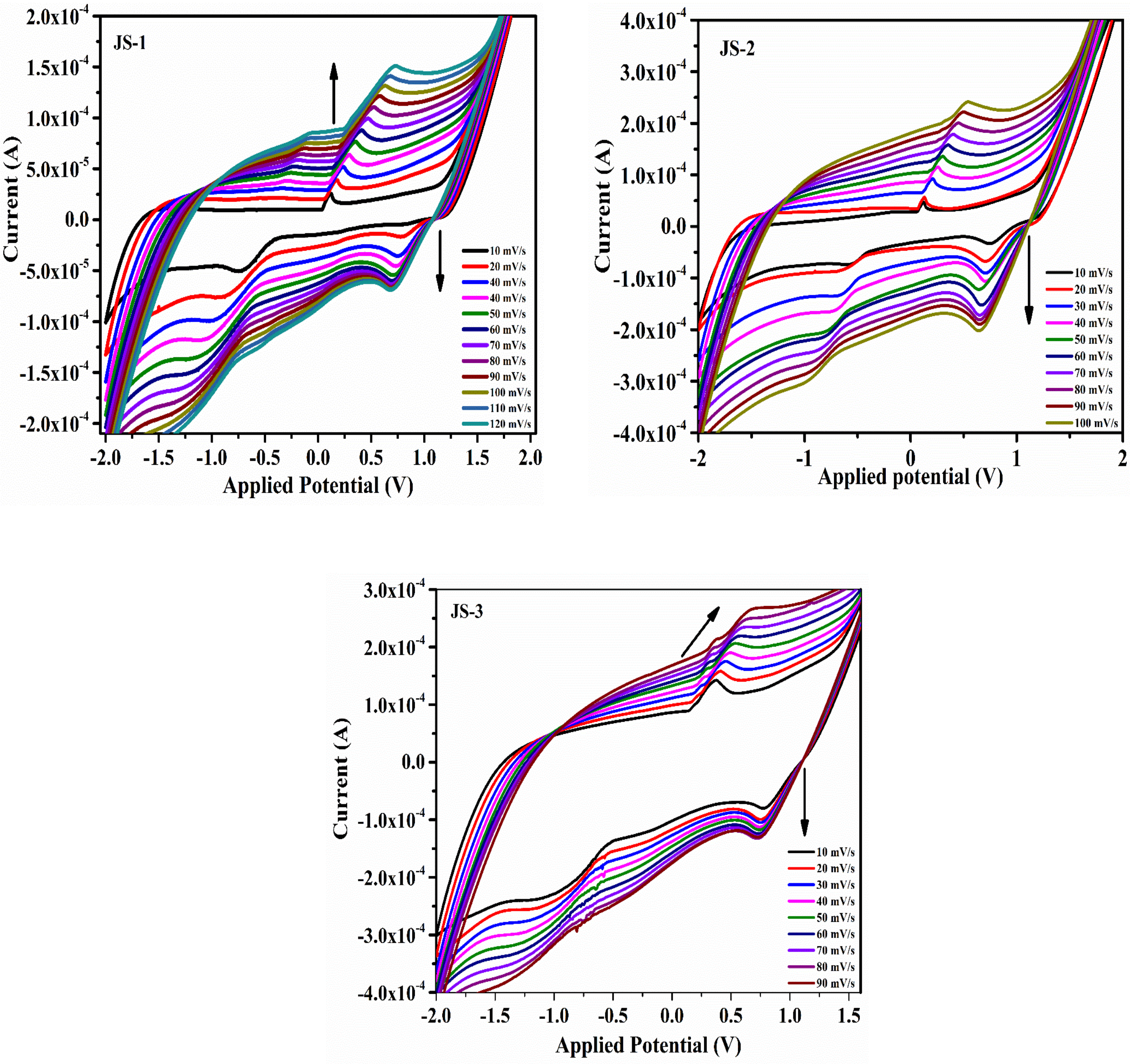


Fig. 4.5: Cyclic voltammograms of series of JS compounds at different scan rates (10 mV/s to 100 mV/s) with KCl (0.1 M) as supporting electrolyte on AgNPs modified SPEs

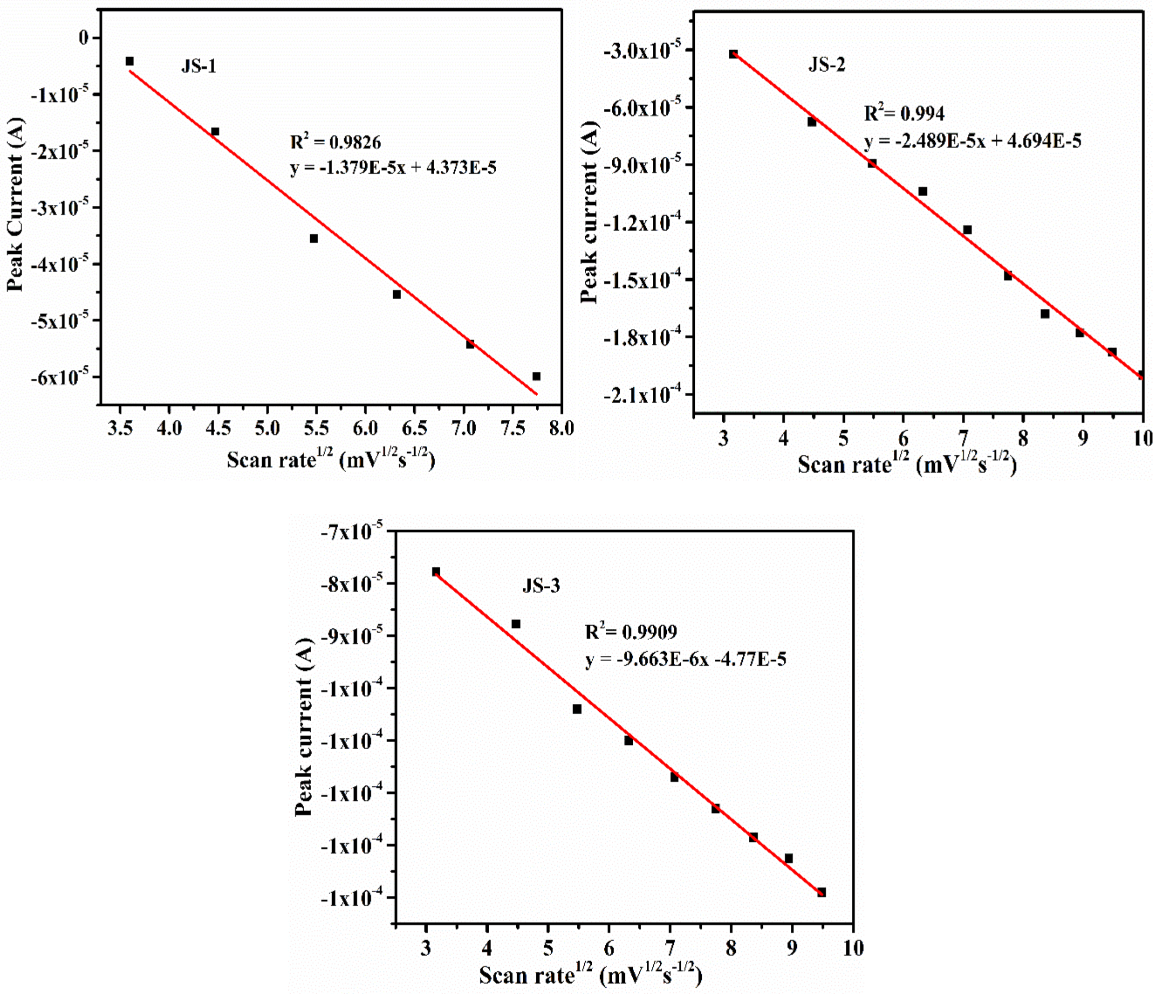


Fig. 4.6: Plots of peak currents vs. square root of scan rates of the JS compounds.

4.3 Metal ion study of JS-1

The prime importance of voltammetry lies in the quantitative detection of the analyte species which can form a strong complex with the ionophore. A change in current with change in concentration can be related for the quantitative detection of the analyte species. The cation receptor properties of JS-1 were studied by cyclic voltammograms in the presence of various cations like Ca^{2+}, Cr^{2+}, Co^{2+}, Zn^{2+}, Fe^{2+}, Mg^{2+}, Pb^{2+}, Ag^{+}, Hg^{2+}, Na^{+}, Cd^{2+} and Al^{3+}. All the cyclic voltammetry scans were carried out at a scan rate of 20 mV/s with KCl (0.1 M) as supporting electrolyte on the AgNPs modified SPEs.

Significant changes were observed on addition of Al^{3+} into JS-1 as shown in Fig. 4.7. All other cations did not show any significant shift in anodic or cathodic peak potential. Hence, J-1 was further studied with different concentrations of Al^{3+}.

Experimental results of the metal titration of JS-1 with Al^{3+} indicated changes in the peak potential in cyclic voltammograms. On sequential addition of 10 µL Al^{3+} to JS-1 modified SPE with KCl (0.1 M) as supporting electrolyte, the cathodic peak potential at 0.71 V begin to diminish, whereas a new anodic peak potential appears at 0.73 V as shown in Fig. 4.8.

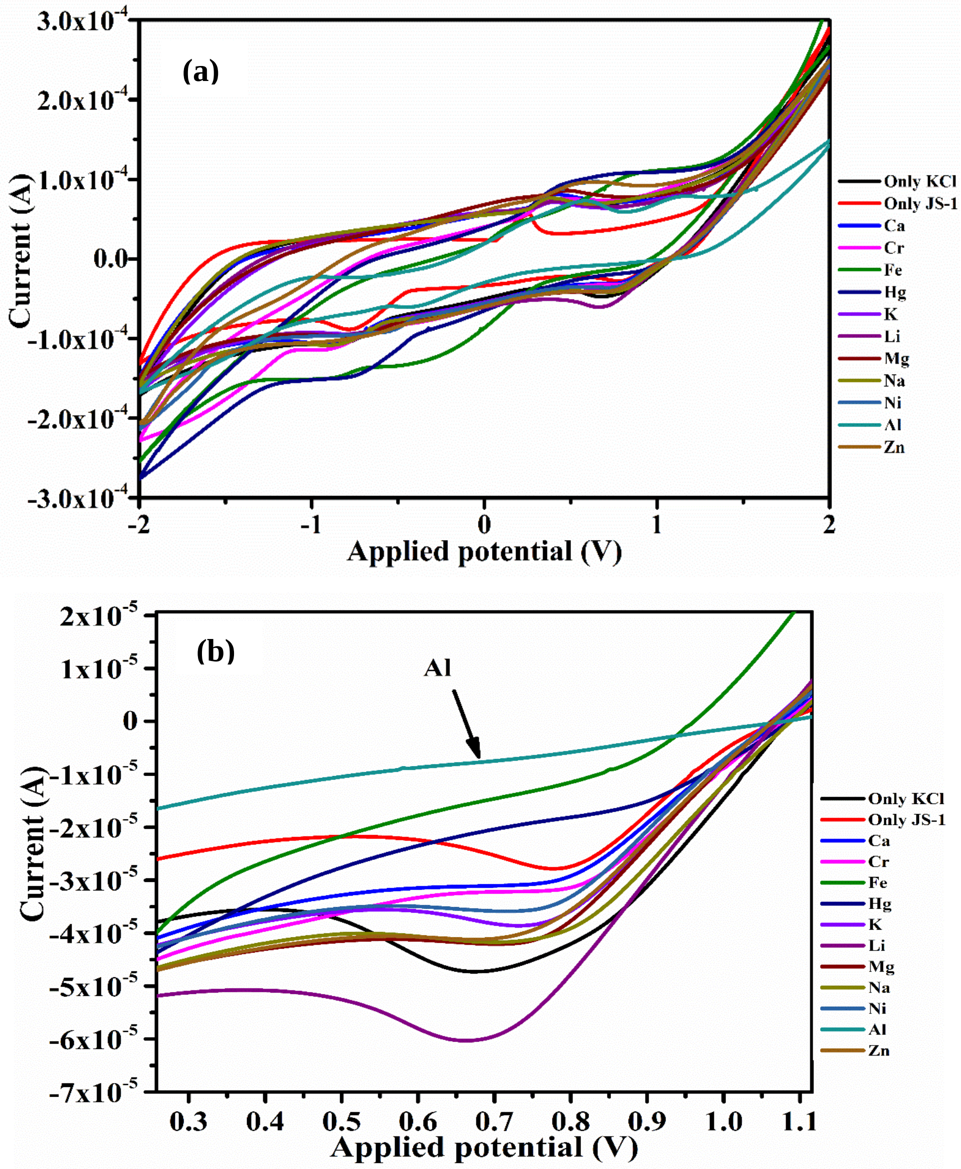


Fig. 4.7: (a) Plot of cyclic voltammograms of JS-1 with different metal ions with KCl (0.1M) as supporting electrolyte on the AgNPs modified SPEs. (b) Shows that the peak disappears for Al(III) at 0.71 V

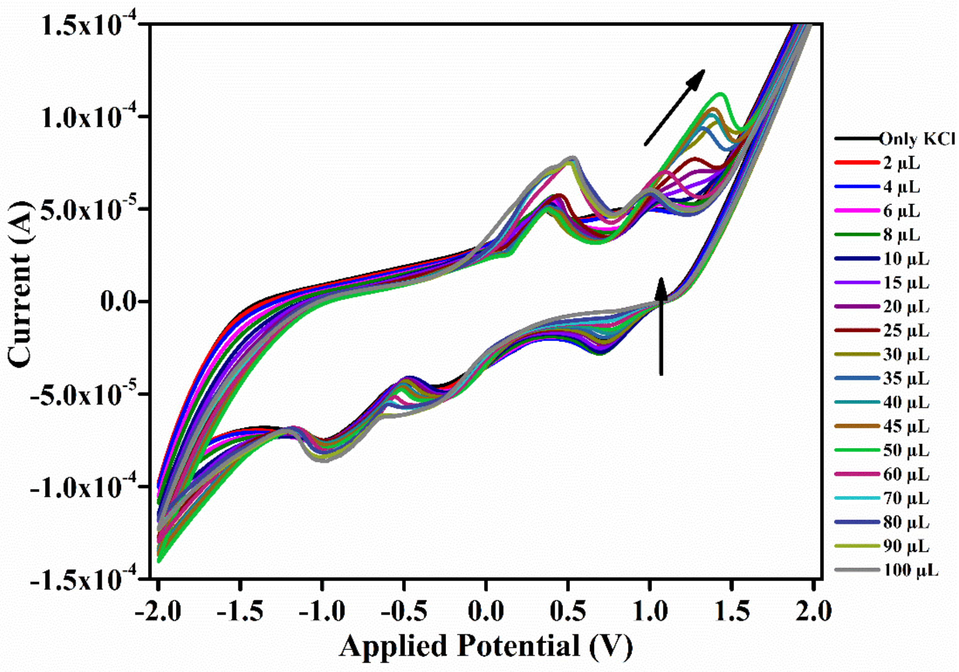


Fig. 4.8: Plot of cyclic voltammograms of JS-1 and AgNPs modified SPEs with different concentrations of Al (III)

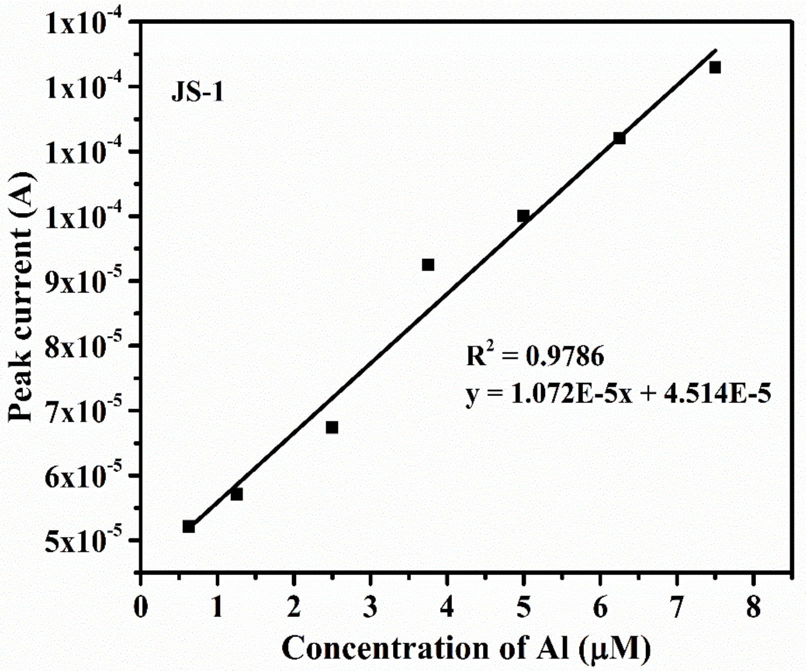


Fig. 4.9: Plot of peak currents vs. different concentrations of Al(III)

The cathodic peak currents increases with concentration as shown in Fig. 4.9. The calibration curve is a linear straight line with a slope of 1.072 × 10^{-5} M.

4.4 Interference of metals with $[JS\text{-}1\text{-}Al]^{+3}$ Complex

Further voltammetric studies of JS-1 with Al^{3+} were carried out in the presence of other interfering metal ions to check the selectivity of the proposed sensor for Al^{3+} ions. Complex of $[JS\text{-}1\text{-} Al]^{3+}$ showed an anodic peak at 0.90 V. Upon addition of other metal ions, there was no significant change in peak potential except for Fe^{3+} ions. In case of Fe^{3+} ions, a new peak at -0.45 V was observed as shown in Fig. 4.10. Hence, most of the transition metal ions did not show any interference except Fe^{3+} and the proposed sensor was selective for Al^{3+} ions.

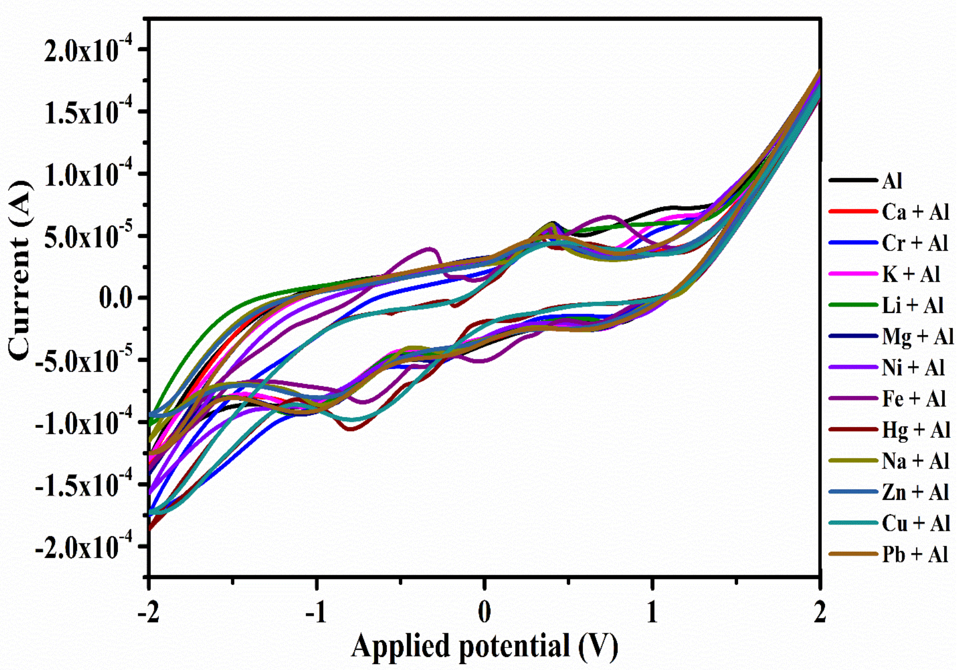


Fig. 4.10: Cyclic voltammograms of JS-1 – Al^{3+} complex in presence of different metal ions (10^{-3} M) as interfering species with KCl (0.1 M) as supporting electrolyte on AgNPs modified SPE

4.5 Real life sampling

To justify the practical applications of the proposed sensor, real-life sampling was done with green tea and Ganga River water which contained Al(III).

Al^{2+} detection from green tea

Green tea sample (0.5 g) was dried and crushed properly in mortar- pestle. The sample was taken in porcelain flask and placed in a heating muffle furnace at 450 °C for 4 hours to remove all the organic matter. After cooling, the sample obtained was dissolved in HNO_3

(5% v/v) aqueous solution and was further diluted with double distilled water.[62] The prepared sample was then analyzed by the proposed method and also with Atomic Absorption Spectroscopy (AAS).

Al^{3+} detection from Ganga river water

Ganga river water was taken into a 100 mL calibrated flask and its pH was adjusted to 1.0 using concentrated nitric acid. The solution was allowed to stand for 24 hours to convert all Al(III) into reactive aluminium.[63] The sample was analyzed with the sensor and AAS.

Table 4.1: Comparison of Al^{3+} concentration in real life samples using proposed sensor and AAS method.

Sample	**Concentration of Al^{3+} (µM) (±SD)**	**Concentration of Al^{3+} (µM) (±SD)**
	Proposed method	**AAS method**
Green tea	1.51 (±0.5)	1.60 (±0.6)
Ganga river water	1.24 (±0.4)	1.30 (±0.4)

4.6 Conclusions

A new voltammetric sensor based on Schiff base derivatives and silver nanoparticles modified screen printed electrodes was developed and its selectivity and sensitivity towards different metal ions were examined. Voltammetric studies carried out in presence of many metal ions indicated that JS-1 was highly selective for Al^{3+}. The limit of detection was found to be 0.82 µM. High sensitivity, low detection limit and the advantage of in-situ application allow the quantitative determination of Al^{3+} in real life samples such as green tea and Ganga river water (Table 4.1).

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