



## Citrus Limon peel as a component of modified carbon paste electrode for electrochemical stripping analysis of Pb (II) and Cd (II)

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### Abstract

Present communication elucidates the development of carbon paste electrode modified with Citrus limon peel for voltammetric analysis of Pb (II) and Cd (II). The metal ions were pre-concentrated at open circuit on the surface of modified sensor, accompanying their determination by stripping voltammetry anodic scan using differential pulse waveform. Electrochemical impedance spectroscopy indicated diminution of charge transfer resistance with higher electrocatalytic response of the modified sensor, supported by cyclic voltammetry measurements. The fabricated metal sensor performance was analyzed by varying the operational conditions like amount of modifier, accumulating solvent and its pH, accumulation time and supporting electrolyte to realize the optimum parameters. The effect of interfering metal ions and surface active macromolecules on the analysis of lead and cadmium was also studied. The linearity was observed in the concentration range of 100-1000  $\mu\text{gL}^{-1}$  for lead and 100-800  $\mu\text{gL}^{-1}$  for cadmium with limits of detection 59.5 and 64.4  $\mu\text{gL}^{-1}$ , respectively at 10 min accumulation time. Thus, the electrode dynamic parameters can be effectively applied for ultra trace determination of lead and cadmium ions being highly sensitive. This work is a green approach in the context of using an environment friendly modifier resulting in improved sensor sensitivity to heavy metal analysis.

**Keywords:** Carbon paste electrode, Citrus Limon, Stripping, Voltammetry, Lead, Cadmium.

### Introduction

Heavy metals coming from different natural and anthropogenic sources have been contaminating our natural water bodies. They are toxic in free elemental form and also in chemically associated forms. Among these metals lead and cadmium are of major concern. Lead and cadmium are heavy metals which are non-degradable and therefore persistent as they find their way in various ecosystems by sources like electroplating, mining, smelting, pigments for plastic, etc<sup>1</sup>. Acute poisoning with lead can lead to permanent damage accompanied by encephalopathy and neurobehavioral-intelligent deficit in moderate lead poisoning cases<sup>2</sup>. Cadmium toxicity can lead to kidney or renal irregularity, bone fraction, elevated blood pressure and ruination of erythrocytes<sup>3</sup>. Hence, constant monitoring of heavy metals at trace level is a critical requirement.

The most common techniques employed for the heavy metal analysis are atomic absorption/emission spectrophotometry and mass spectrometry<sup>4,5</sup>. These techniques are expensive, time devouring, require experts to operate them and are not portable. They sample pretreatment is a pre-requisite for most of these techniques rendering the analysis laborious<sup>6</sup>. As a result, electrochemical methods using carbon paste electrodes (CPEs) with modifiers have attracted attention for voltammetric analysis of trace metals<sup>7</sup>. A modified CPE (MCPE) is advantageous because of enhanced response, convenient fabrication, lower cost and ease for miniaturization<sup>8</sup>. Crown

ether, 2, 4 dinitrophenylhydrazine, quercetin, cobalt phthalocyanine and antimony trioxide are some chemicals which have been used for the modification of carbon paste electrode<sup>9-13</sup>. The toxic effects of these chemicals limit their application as a modifier.

The attention thus shifted to search for modifiers that would be eco-friendly and yet sensitive for electrochemical analysis of metals. The usage of trash plant parts as modifiers for CPE is credited to the presence of electrochemically or chemically active moiety in them, with certain functionalities or donor groups<sup>14</sup>. Citrus limon peel was utilized for modifying CPE to achieve sensitive determination of Pb(II) and Cd(II). Citrus Limon peel is basically an agricultural waste and is constituted mainly of essential oils, cellulose, vitamin C and flavonoids<sup>15-17</sup>. The present study demonstrates household kitchen waste Citrus limon peel's utility for modifying carbon paste sensor to enhance its sensitivity for Pb (II) and Cd (II) determination. According to the best of our knowledge this is the first attempt to use Citrus limon peel to modify CPE for heavy metal estimation.

### Materials and methods

**Apparatus:** All electrochemical measurements were done using  $\mu$  Autolab Type potentiostat (Type III, Purchased from Ecochemie, Netherlands) and NOVA 1.8 software. The three electrode set-up (standard) was used with working electrode

being *Citrus limon peel* modified carbon paste electrode (CPMCPE), counter being Pt wire and Ag|AgCl (3M KCl) as reference electrode. The pH measurements were carried out on a digital pH meter (Mettler Toledo) containing saturated calomel electrode (reference) and a glass electrode, pre-standardized with standard buffers. All the measurements were made at room temperature ( $25 \pm 1$  °C). For electrochemical impedance study FRA module was used.

**Chemicals and Reagents:** Graphite powder (<20 $\mu$ m), light mineral oil, lead and cadmium nitrate ( $\geq 99\%$ ), potassium chloride ( $\geq 99\%$ ), potassium hydroxide ( $\geq 90\%$ ), sodium hydroxide ( $\geq 97\%$ ) were procured from Sigma-Aldrich. Test solutions were prepared from the stock solutions of lead and cadmium (1000  $\mu$ g/ml). Potassium phosphate, boric acid (99%), perchloric acid, nitric acid, acetic acid, sulfuric acid and hydrochloric acid were obtained from Merck. ELGA Milli Q ultra purification assembly was utilized for obtaining ultra pure water (resistivity=18M $\Omega$ ). Rest all the chemicals being of analytical grade were utilized without any further purification.

**Preparation of *Citrus limon peel* biomass:** The peel of lemons was collected from the household kitchen trash. The remaining pulp sticking to the peel was taken off and subsequently washed several times with water and then dried. This material was then powdered and sieved using a Cu sieve (mesh size: 150  $\mu$ ). The fine material so obtained was made use of for the fabrication of carbon paste sensor.

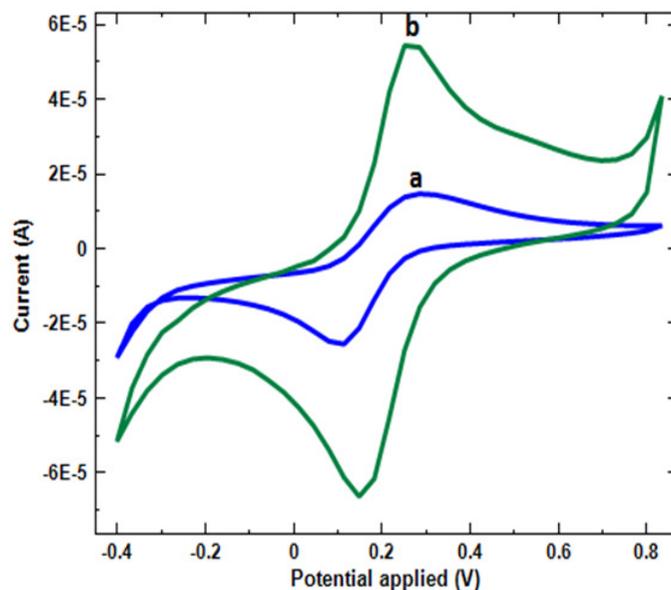
**Fabrication of *Citrus limon peel* modified carbon paste sensor:** The unmodified/bare CPE was prepared without *Citrus limon peel* biomass. The *Citrus limon peel* modified CPEs (CPMCPE) were prepared by evenly mixing *Citrus limon peel* biomass in varying amount (2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 30 and 40 % w/w ratio) with 0.3 g carbon powder (Graphite), while using 100  $\mu$ L mineral oil (Nujol) as a binder. The mixture was homogenized to obtain a smooth paste, which was subsequently packed into a hollow cylindrical tube made of glass with 0.3 cm diameter. For the electrical contact, Cu wire was utilized. The sensor's surface was polished on a photo paper to get a smooth surface. The electrodes so prepared were left to dry in a desiccator overnight before being applied for analysis. They were then stored in a refrigerator for use henceforth.

**Procedure:** The electrode surfaces were activated by the pre-treatment carried out by the cyclic voltammetry in 0.1M HCl by cycling (~20 cycles) between -1 V to +1 V at the step potential 0.00244 V and 100 mV/s scan rate. The cyclic voltammogram revealed that just the residual current existed in the potential range of -1 V to +1 V which suggested that the electrodes can be used within this range. After pre-treatment, electro-active surface area was found to increase, which was attributed to amplified current response for the voltammetric estimation of cadmium and lead. Differential pulse anodic stripping voltammetry (DPASV) technique (scan rate of 50 mV/s and

pulse amplitude being 100 mV) was employed for quantitative measurements in order to realize sensitive trace analysis. It comprised of two steps, wherein, accumulation was carried out under open circuit conditions, i.e. the modified sensor was dipped in metal solution followed by rinsing with water. Subsequently, the medium was exchanged to carry stripping analysis. The sensor was kept immersed during the experiment in HCl solution (0.1 M) and EDTA (0.1 M) was used for regeneration.

## Results and discussion

**Characterization (Electrochemical) of CPMCPE:** Cyclic voltammetry (CV) was performed to elucidate changes in the sensor response on modification. Figure-1 depicts cyclic voltammograms obtained for unmodified CPE (curve a) and CPMCPE in 5 mM  $K_3[Fe(CN)_6]$  (curve b). The redox peak currents were found to increase at CPMCPE in comparison to unmodified CPE and also decrease in the peak potential difference was noticed. CV results indicate enhancement in the current response with CPMCPE due to enhanced electron transfer process.



**Figure-1:** CV curves for unmodified CPE (a) and CPMCPE (b) in ferricyanide solution (5 mM in 0.1 M KCl) at 50 mV/s scan rate.

**Electrochemical response of lead and cadmium at CPMCPE:** CV was performed to study the lead and cadmium uptake by CPMCPE. No peak was observed in the cyclic voltammogram measured in 0.1 HCl solution, when no accumulation was carried out prior to it (Figure-2, curve a). Well defined oxidation peaks were realized on accumulation for 10 mins, which is an indication of these metals being accumulated at the surface of electrode and stripping response was observed when scanned in anodic direction (Figure-2, curve b).

Based on CV results, DPASV was used to characterize the modified electrode. The DPASV scan of unmodified electrode showed no peak implying the lack of sufficient pre-concentration of Pb (II) and Cd (II). On contrary, when CPMCPE was used, symmetric and defined anodic stripping peaks at a potential of -486 mV and -713 mV were obtained corresponding to oxidation of Pb (II) and Cd (II), respectively (Figure-3).

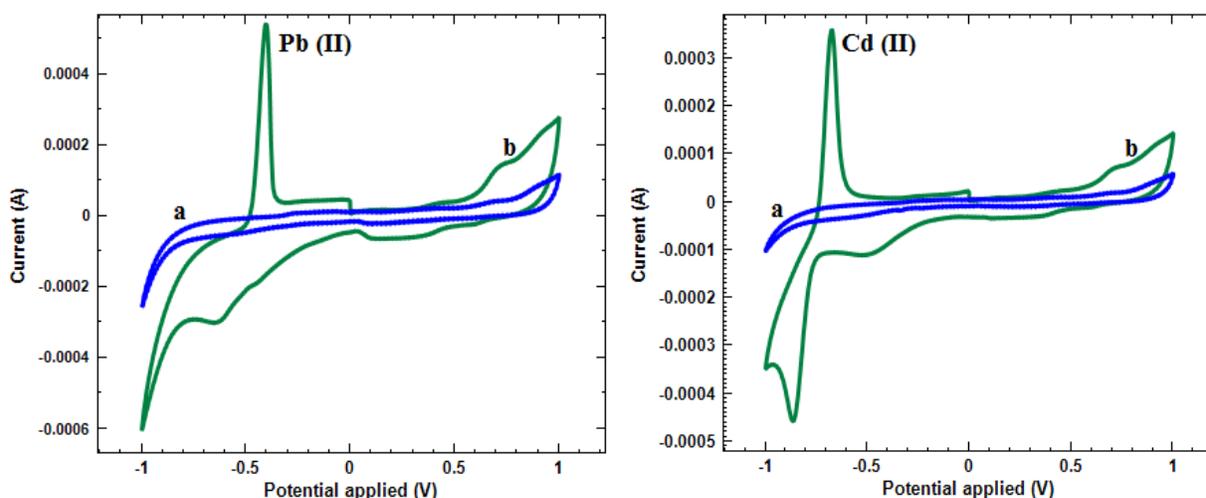
**Effective surface area:** CV was carried out at scan rates varying from 10-100 mV/s in  $K_3[Fe(CN)_6]$  solution (1 mM). The electroactive surface area of the sensor was calculated using Randles-Sevcik equation<sup>18</sup>.

$$I_p = (2.69 \times 10^5) AD^{1/2} n^{3/2} \gamma^{1/2} C \quad (1)$$

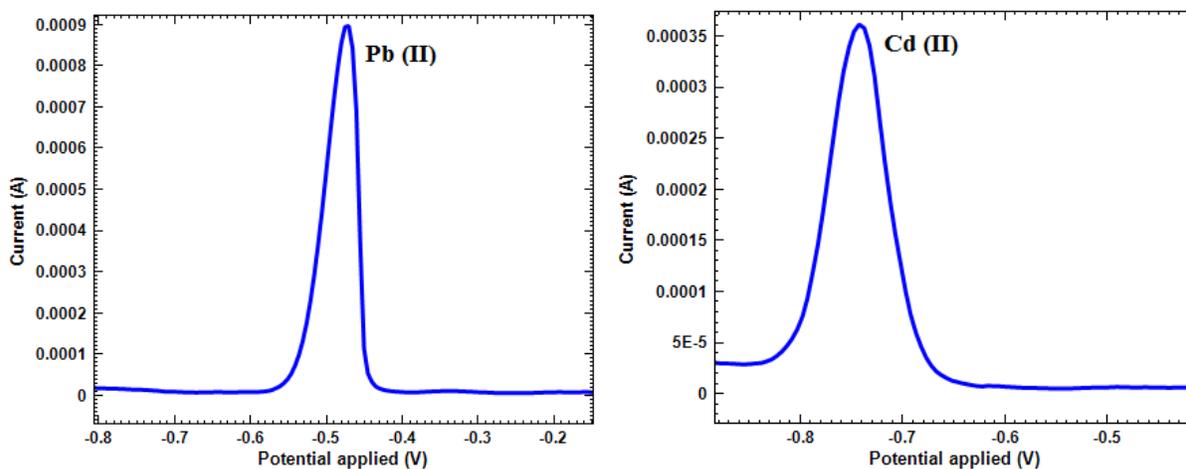
Where: n corresponds to number of electrons involved in the oxidation-reduction process, A signifies electroactive surface area of the sensor ( $cm^2$ ), D stands for diffusion coefficient of

analyte in the solution ( $cm^2 s^{-1}$ ), C stands for concentration of analyte present in bulk solution ( $mol cm^{-3}$ ), and  $\gamma$  is indicative of the scan rate ( $V s^{-1}$ ). The effective surface area came out to be  $0.369 cm^2$  for CPMCPE as compared to  $0.154 cm^2$  for unmodified CPE.

**Electrochemical impedance study:** The enhancement in the electron transfer process at CPMCPE was also scrutinized using electrochemical impedance spectroscopy. For the analysis, an AC (amplitude:10 mV) in the frequency range 1-1000 Hz was applied. The higher electrocatalytic behavior of CPMCPE was confirmed by a decrement in charge transfer resistance. The charge transfer resistance values were obtained by fitting an appropriate equivalent circuit (Randles circuit), and thereby found to be 20.3 K $\Omega$  at unmodified CPE and 182  $\Omega$  at CPMCPE. Thus we see that on modification charge transfer resistance is reduced, which is in accordance with the result of surface area enhancement (Figure-4).



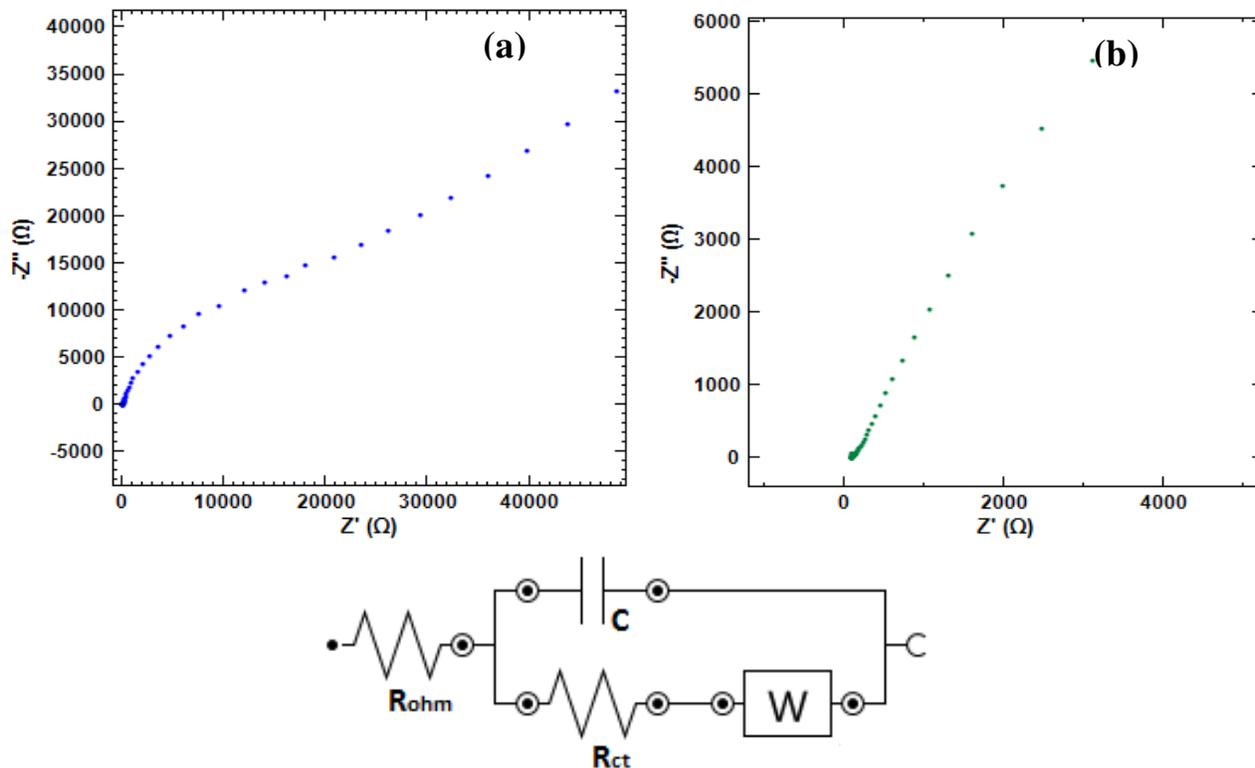
**Figure-2:** Cyclic voltammograms recorded at CPMCPE in HCl (0.1 M) with no accumulation (a); on accumulation of Pb (II) and Cd (II) for 10 mins (b) at 50 mV/s scan rate.



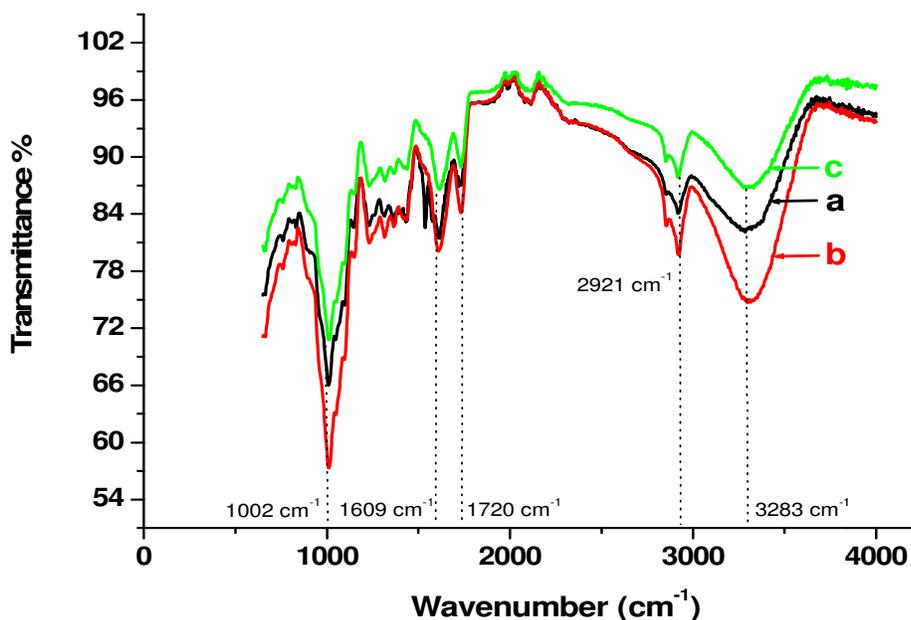
**Figure-3:** DPASV performed in 0.1 M HCl for determination of Pb (II) and Cd (II) on accumulation for 10 mins.

**FTIR Analysis:** The adsorption of metal ions on the lemon peel biomass confined at the surface of electrode is explained on the basis of electrostatic interaction between metal ions and functional moieties present in plant material. Ionization of the functional groups in aqueous solutions allows them to bind

cations. FTIR studies were thus undertaken to understand the interaction of metal ions with functional moieties existing in biomass. FTIR spectra of lemon peel biomaterial before and after adsorption of lead and cadmium are shown in Figure-5.



**Figure-4:** Nyquist plots recorded at unmodified CPE (a) and CPMCPPE (b) in 5 mM ferricyanide solution and equivalent electrochemical circuit.



**Figure-5:** FT-IR spectra of untreated biomass (a), on treatment with lead (b) and cadmium (c).

The FTIR spectra of untreated lemon peel biomass showed absorption at  $3283\text{ cm}^{-1}$ ,  $2921.8\text{ cm}^{-1}$ ,  $1720.4\text{ cm}^{-1}$ ,  $1609\text{ cm}^{-1}$  and  $1002\text{ cm}^{-1}$  which is ascribed to hydroxyl group, stretching vibration of C—H, C=O stretching vibration, bending vibration of N—H (amide group), and C—O intense absorption in fingerprint zone, respectively. After treatment with Pb (II), peak positions shifted to  $3302.5\text{ cm}^{-1}$  (—OH),  $1734\text{ cm}^{-1}$  (carbonyl bond stretch),  $1610.3\text{ cm}^{-1}$  (bending of N—H in the amide) and  $1005.7\text{ cm}^{-1}$  (C—O). Similarly on treatment with Cd (II), the peaks were obtained at  $3291.7\text{ cm}^{-1}$  (—OH),  $1734\text{ cm}^{-1}$  (carbonyl bond stretch),  $1607.4\text{ cm}^{-1}$  (bending of N—H in the amide) and  $1015.5\text{ cm}^{-1}$  (C—O). Difference in intensity of peaks on treatment of biomass with metal ions was also observed. On treatment with Pb (II), band intensities increased, indicating stretching of —OH and C—O bonds, whereas on treatment with Cd (II) band intensities decreased implying hindrance in stretching of these bonds. In essence the FTIR analysis indicates interaction of the amide, hydroxyl, carboxylate and carbonyl groups with lead and cadmium.

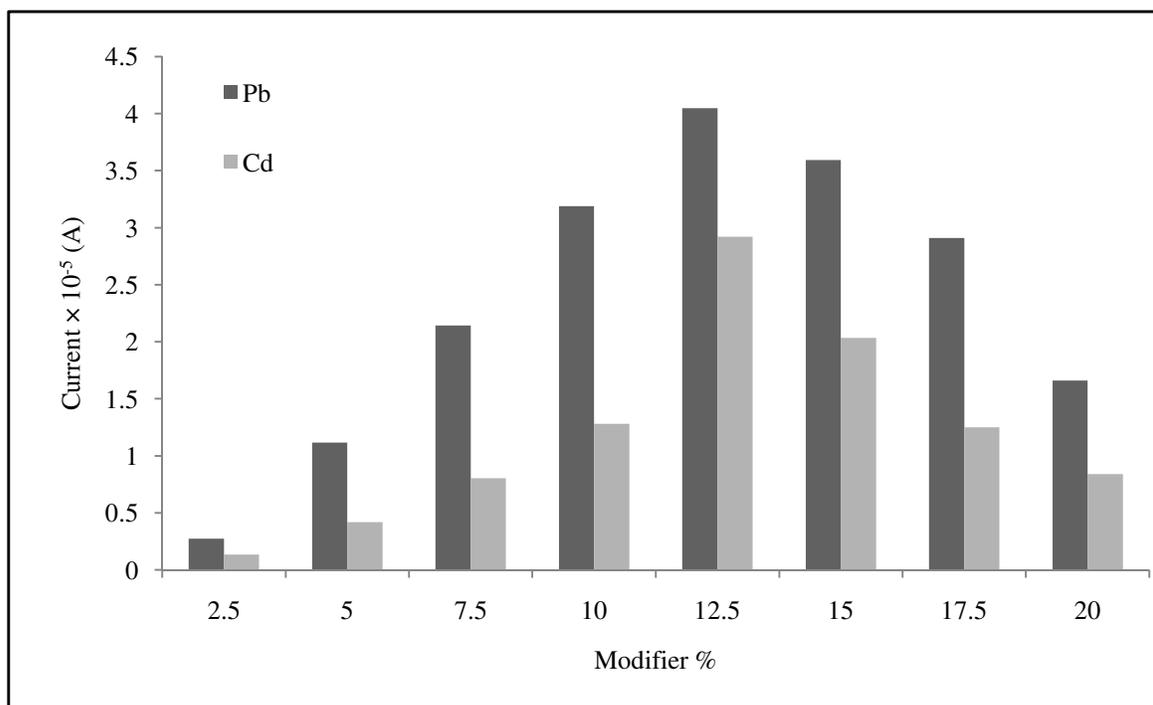
**Operational parameters optimization:** The voltammetric response of fabricated sensor was investigated in reference to stripping parameters, i.e. the influence of modifier percentage, accumulating media, pH of accumulating media, supporting electrolyte and accumulation time. These electrochemical parameters were optimized in terms of current response for estimation of lead and cadmium at CPMCPPE using DPASV.

**Amount of modifier:** The modified electrode's current response for lead and cadmium in reference to biomass/graphite

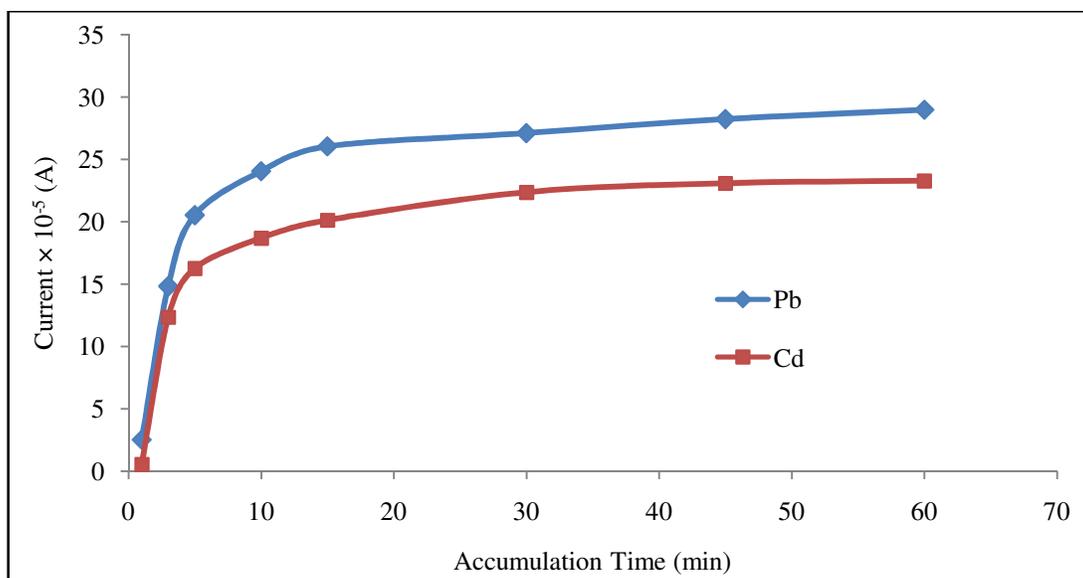
ratio was scrutinized by varying modifier amount from 2.5% to 40% (w/w). An increment in the peak current was realized till 12.5% of biomass to graphite ratio (Figure-6), which is ascribed to an increment in the available sites for metal ions adsorption on the sensor's surface. With further increase in percentage of the modifier, peak current was found to diminish, which is evident on account of exceeding non conducting sites in comparison to the active sites at higher biomass concentration.

**Time of accumulation:** The duration of electrode surface exposure to the analyte solution marks a crucial parameter. The current response was found to increase with the pre-concentration time upto 15 mins, thereafter prolonged accumulation did not result in any enhancement of peak current. This is because at a lengthy deposition time, the analyte saturates at the surface of electrode and thus results in no more improvement in the current response (Figure-7). With extended accumulation time, fouling of the electrode surface can occur which affects the electrode's sensitivity. The time for accumulation was thus optimized at 10 mins considering both the sensitivity and analysis time length.

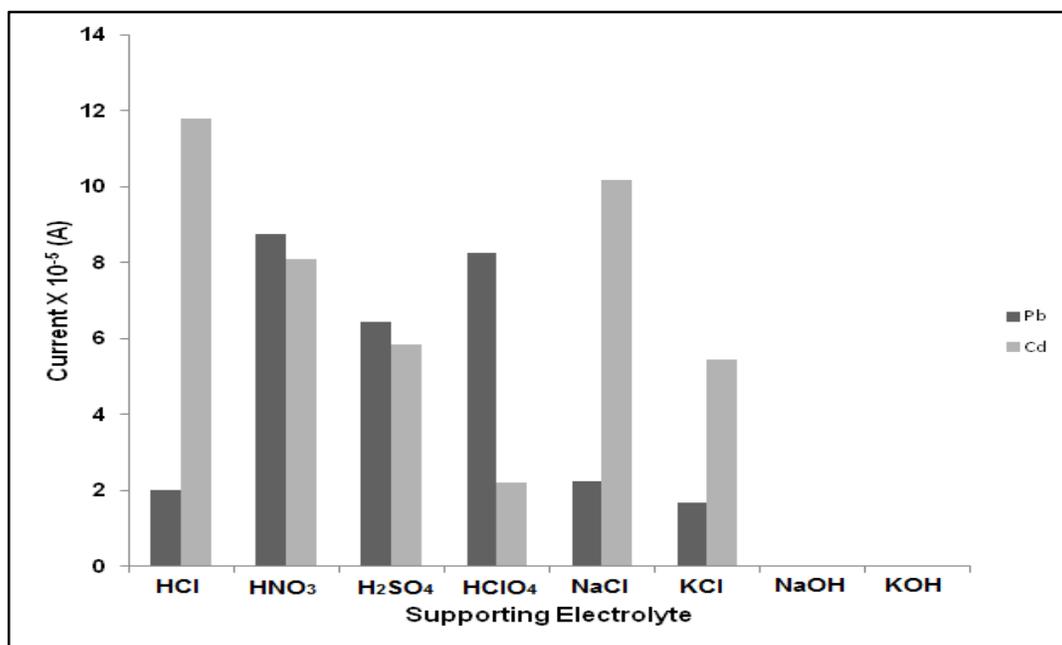
**Supporting electrolyte:** The effect of supporting electrolyte on voltammetric current response of metal ions at the modified sensor was analyzed and found to have an influence on the peak position and height (Figure-8). Further, the metal ion determination was done at varying supporting electrolyte concentration ranging from 0.01-1 M to study its effect. For Pb (II), best results were obtained with 0.1 M  $\text{HNO}_3$  as supporting electrolyte and for Cd (II) with 0.1 M HCl.



**Figure-6:** DPASV current response of cadmium and lead ( $1\text{ }\mu\text{g/ml}$ ) using different biomass percentage; accumulation time being 10 min; supporting electrolyte, 0.1 M HCl; scan rate of 50 mV/s and 25 mV pulse amplitude.



**Figure-7:** Effect of accumulating electrolyte on DPASV current response of lead and cadmium (1  $\mu\text{g/ml}$ ) for accumulation of 10 min at CPMCPE.



**Figure-8:** Influence of various supporting electrolytes on current response (DPASV) of lead and cadmium (1  $\mu\text{g/ml}$ ) at CPMCPE for 10 mins of accumulation.

**Accumulating media (Effect of pH):** The interaction of metal ions with different functional groups on *Citrus limon* peel biomass modified surface can be assessed from FT-IR results. The functional groups ionization on the biomass surface is dependent on the solution, most of these functional groups being ionized at  $\text{pH} > \text{pK}_a$ . Thereby, influence of accumulating media on the current response was studied. In acidic medium, no voltammetric peak was observed, which can be due to the protonation of functional groups present in modifier resulting in diminished ability for complexing. The metal accumulation was

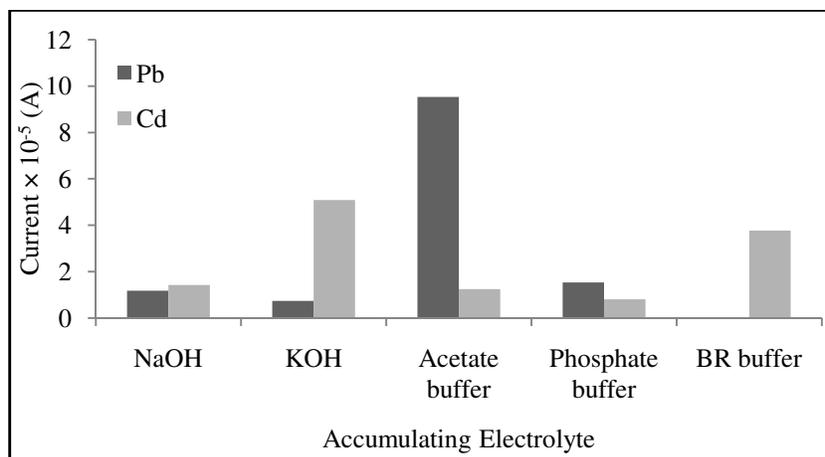
probed using supporting electrolytes like phosphate buffer, acetate buffer and Britton-Robinson (BR) buffer. The concentration of the accumulation media, which showed maximum voltammetric response, was also optimized. Acetate buffer showed a well defined peak for lead and thus the pH of acetate buffer was optimized for it and in case of cadmium bases showed a good current response (Figure-9). 1mM pH 6 acetate buffer gave a maximum current response for lead and 30 mM KOH for cadmium.

**Interference Study:** One of the key features of modified electrode is its selectivity for metal ions. The effect of other interfering ions existing in the solution on current response of cadmium and lead ions was analyzed. Not much interference for lead was observed till twenty fold cadmium, ten fold mercury, hundred and fifty fold zinc, fifty fold copper and two hundred fold chromium. For cadmium no interference was noticed up till twenty five fold lead, fifteen fold mercury, two hundred fold zinc, hundred fold copper and one hundred fifty fold chromium. Besides slight mutual interference there is no significant interference from other metal ions.

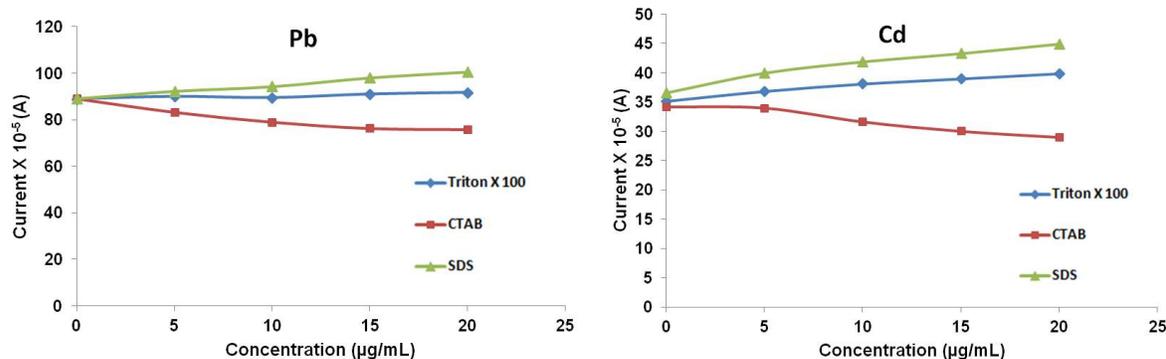
**Surfactant study:** Triton X-100, cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were chosen as representatives of nonionic, cationic and anionic surfactants to study their effect on the determination of lead and cadmium ions at CPMCPPE. The same electrode's surface was renewed for each measurement to study the effect of surfactant with increasing concentration. The influence of surfactant concentration on the current response is depicted in Figure-10 for both lead and cadmium analysis. A decline in the peak current was realized in the presence of CTAB which is a

cationic surfactant. For SDS, an elevation of the peak current value was noticed. In contrast, not much noticeable change was realized with Triton X 100 which is a nonionic surfactant. These results are in agreement with electrostatic interaction being responsible for attachment of metal ions on the surface of electrode.

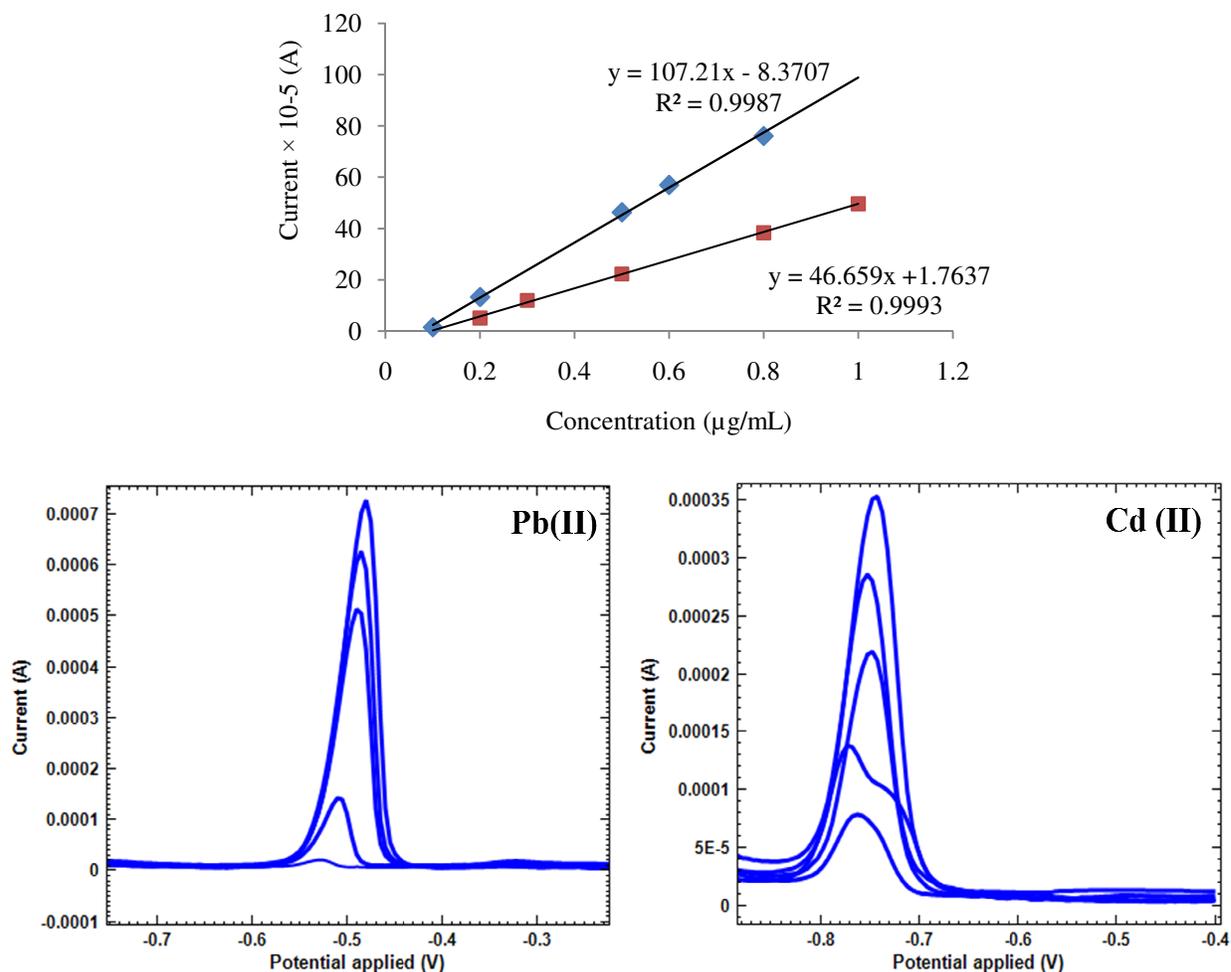
**Analytical parameters and validation of method:** The fabricated sensor's analytical performance for increasing concentrations of lead and cadmium ions under the optimum conditions was investigated. The linearity between the concentration and corresponding peak current in the range of 100-800  $\mu\text{gL}^{-1}$  for Pb (II) and 100-1000  $\mu\text{gL}^{-1}$  for Cd (II). The calibration curve so obtained was found to follow the regression equation,  $Y = 107.21x - 8.3707$  [regression coefficient ( $r^2$ ) = 0.999] and for cadmium,  $Y = 46.659x + 1.7637$  [regression coefficient ( $r^2$ ) = 0.999]. The limit of detection (LOD) is evaluated to be 59.485  $\mu\text{gL}^{-1}$  (S/N=3) for Pb (II) and 64.399  $\mu\text{gL}^{-1}$  (S/N=3) for Cd (II) after an accumulation time of 10 mins. The limit of quantification was found to be 198.28  $\mu\text{gL}^{-1}$  and 214.66  $\mu\text{gL}^{-1}$  for Pb (II) and Cd (II), respectively, under optimized conditions (Figure-11).



**Figure-9:** Effect of accumulating electrolyte on the current response (DPASV) of lead and cadmium (1  $\mu\text{g/ml}$ ) at CPMCPPE for 10 mins of accumulation.



**Figure-10:** Influence of various surfactants with increasing concentration on DPASV current response of lead and cadmium (1  $\mu\text{g/ml}$ ) at CPMCPPE in HCl for accumulation of 10 mins.



**Figure-11:** Standard calibration plot for lead and cadmium ions obtained for accumulation of 10 mins under the conditions optimized.

Reproducibility of method proposed was analyzed by repetitive measurement (ten times a day) of metal ions as described for intra-day precision and for inter-day precision check, for which measurements (triple) were made for 4 days. The results were found to be convincingly reproducible with a relative standard deviation less than 2 % for intra-day analysis and not more than 3 % for inter-day analysis.

The analysis was carried out using a single modified sensor (CPMCPE) for every five days over a period of month and maximum deviation realized was about 3.0 %. The fabricated sensor thus offers sensitive analysis and it also gives a stable response.

## Conclusion

A new carbon paste sensor was prepared by using *Citrus limon peel* as a modifier for the preparation of MCPs. The fabricated CPMCPE offers several advantages such as simple preparation, high stability, uniformity in composite paste, long life time and

reproducibility. The *Citrus limon peel* was used as a modifier material without any pre-treatment. The detection limit of the proposed modified electrode is  $59.485 \mu\text{gL}^{-1}$  and  $64.399 \mu\text{gL}^{-1}$  respectively, for Pb (II) and Cd (II) which is lowest reported for any plant modified carbon paste electrode. FT-IR analysis showed that functional groups present in the plant material were involved in metal binding. An enhanced current response in the presence of anionic surfactants was realized for the lead and cadmium analysis. Despite slight mutual interference CPMCPE has proved to be a better sensor. Thus, CPMCPE can be applied for sensitive electrochemical determination of trace metals and it offers a green route as compared to use of mercury electrodes.

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