

Removal of Zinc from Wastewater through the Reduction Potential Determination and Electrodeposition Using Adsorption-Desorption Solutions

Issabayeva, Gulnaziya⁺; Yap Junmin, Nicholas*

Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman (UTAR), MALAYSIA

Ajeel, Mohammad A.

Department of Environment, Faculty of Environment and Energy, Al-Karkh University of Science, IRAQ

*Hussin, Farihahusnah; Aroua, Mohamed Kheireddine**

Centre for Carbon Dioxide Capture and Utilisation, school of Science and Technology, Sunway University, MALAYSIA

ABSTRACT: *The rubber product manufacturing industry generates large volumes of wastewater containing on average 10 ppm of zinc. Presently, zinc is removed via a chemical precipitation process generating hazardous precipitate that requires secure disposal. This study evaluated the removal of zinc through adsorption on Palm Shell Activated Carbon (PSAC) and subsequent desorption in hydrochloric, nitric (0.1 and 0.2 M) and citric (0.2 and 0.5 M) acids to produce solutions for the electrodeposition of zinc to achieve the permissible discharge level of 2 ppm. The highest desorption efficiency was achieved using HCl. Cyclic Voltammetry (CV) was applied to determine the reduction potential of zinc in desorption solutions. The presence of KCl and a buffer solution improved the electrodeposition of zinc. The chloride-based solution showed the best electroreduction behavior of zinc with a well-defined reduction peak as compared to the nitrate and citrate-based solutions, with a wider reduction peak and no peak, respectively. The chloride-based solution, selected for the electrodeposition experiments, showed 64 % reduction in zinc concentration within 10 min. The prolonged to 30 min electrodeposition resulted in only 7 % of further increment. Overall, the obtained results confirm the feasibility of zinc removal through the electrodeposition from the adsorption-desorption solution, which provides an effective alternative to the currently industrially used chemical precipitation method.*

KEYWORDS: *Zinc; CV; Adsorption; Desorption; Palm shell activated carbon; Wastewater.*

INTRODUCTION

Malaysia is one of the leading exporters and producers of rubber based products [1]. Zinc oxide is used in the compounding stage of natural rubber as a cross-linking promoting agent [2]. The excess of zinc is washed away

during the final production stage producing large volumes of wastewater subjected to the chemical precipitation to reduce zinc concentration from about 10 ppm to a permissible discharge level of 2 ppm [3]. Chemical

* To whom correspondence should be addressed.

+ E-mail: gulnaziya@utar.edu.my

• Other Address : Department of Engineering, Lancaster University, Lancaster, UNITED KINGDOM
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precipitation provides effective reduction of zinc concentration below 2 ppm; however, the process requires large volumes of caustic soda and produces insoluble precipitate subjected to the hazardous waste disposal requirements. Application of other separation technologies, for example membrane separation, is hindered due to the high content of SS, BOD and COD in the wastewater. Adsorption can efficiently remove zinc from the wastewater and at lower cost when using agriculture wastes adsorbents. For example, palm shell activated carbon (PSAC) produced from the oil palm shells disposed after palm oil extraction at the plantations in Malaysia [4]. Moreover, the adsorbent can be reused in multiple cycles after the desorption treatment [5]. In turn, solutions with desorbed zinc can be used to recover zinc using an electrochemical technique known for their versatility, energy efficiency, amenability to automation and cost effectiveness [6, 7]. This study investigated the feasibility of zinc removal from aqueous solutions through the adsorption-desorption and electrodeposition processes, including the determination of reduction potentials in CV tests, to meet the wastewater discharge limit.

EXPERIMENTAL SECTION

Batch adsorption experiments

Commercially available Palm Shell Granular Activated carbon (PSAC) was provided by Bravo Green Sdn Bhd, Malaysia. 0.01 M zinc nitrate hexahydrate was used to prepare solutions. 5 g of 0.85-1.0 mm PSAC was added into a 100 mL flask of zinc solution and placed on an orbital shaker (SSL1, Stuart®, Cole-Parmer, UK) at 180 rpm for one hour. The adsorbate solution was filtered (Smith Scientific Limited) and analyzed for Zn concentration using inductively coupled plasma optical emission spectrometer (Optima 7000DV, Perkin Elmer, USA). All measurements were carryout out in triplicates. The initial zinc concentrations of 10, 50 and 100 ppm were tested. The pH of the synthetic wastewater was maintained at pH 5, a typical pH of industrial wastewater in Malaysia [3].

Desorption experiments

0.1 M and 0.2 M solutions of hydrochloric and nitric acids; and 0.2 M and 0.5 M solutions of citric acid were used as desorbing agents. The flasks were agitated on a shaker (LSI-3016A, LabTech, Daihan Labtech Co Ltd, Korea) at 180 rpm for one hour at 25 °C. The initial and final

concentrations of zinc were measured using ICP-OES to determine the desorption efficiency.

Cyclic Voltammetry

To determine effect of KNO_3 and pH buffer solution on electrodeposition of zinc, the CV tests were carried out in the three solutions: i) zinc desorption solution; ii) zinc desorption solution with 0.25 M KNO_3 and iii) zinc desorption solution with 0.25 M KNO_3 and pH buffer. CV experiments were conducted in a three-electrodes electrochemical cell consisted of the counter electrode (platinum wire, area = 0.1 cm^2), reference electrode (Ag/AgCl) and working electrode (stainless steel, area = 0.07 cm^2). Electrochemical reduction behaviour of zinc in different electrolytes was studied using Autolab Metrohm potentiostat with NOVA 1.10 software (PGSTAT302N/MBA, Metrohm, Switzerland).

Zinc deposition

In the electrodeposition of zinc experiments, a 200 mL electrochemical cell with the stainless steel cathode (area = 70 cm^2) and graphite anode (area = 0.1 cm^2) was used. The same electrolyte solutions of pH 4 as in CV tests were used. 100 A/m^2 and 200 A/m^2 current densities were tested using GW Instek laboratory direct current power supply (GPR-16H50D, Taiwan). Deposition duration was set at 10 and 30 minutes. The remaining zinc concentration was measured using ICP-OES.

RESULT AND DISCUSSION

Adsorption of zinc on PSAC

The mean removal efficiency of zinc was 68.29 %, 95.35 % and 98.33 % for the initial concentration of 10 ppm, 50 ppm and 100 ppm, respectively. The amount of zinc adsorbed onto PSAC increased as the concentration of zinc ions increased; however, the difference between 50 and 100 ppm concentrations was small. At 10 ppm, low amount of zinc ions relative to the available number of adsorption sites caused the fractional adsorption to be independent of the initial concentration. Meanwhile at 50 ppm, removal of zinc indicated dependence on the initial concentration due to a higher driving force of mass transfer. However, at 100 ppm, the removal efficiency increased by a small margin of 3 % reaching maximum efficiency of 98 %. Such insignificant increase in zinc adsorption is likely to be associated with the exhaustion of

the adsorption sites in a given dosage of the adsorbent; a trend observed in many adsorption studies [8-11].

Desorption of zinc from PSAC

Table 1 summarises the results on desorption in three different desorbing solutions. More zinc was desorbed in 0.1 M HCl as compared to 0.2 M HCl. It possibly relates to the tendency of zinc to form coordination complexes with chloride and hydroxide ions such as $Zn(OH)^{3-}$, $Zn(OH)_4^{2-}$, Zn_2OH^{3+} , $ZnCl^+$, $ZnCl_3^-$, $ZnCl_4^{2-}$ and $ZnOH^+$ as suggested by the chemical speciation software Visual Minteq 3.1 [12]. Such metal complexes may precipitate on the adsorbent surface preventing subsequent desorption of zinc. The desorption efficiency in 0.2 M nitric acid was higher than in 0.1 M solution, which is attributed to the formation of fewer complexes as compared to HCl solution. Visual Minteq speciation profile indicated presence of the following complexes: $Zn(OH)^{3-}$, $Zn(OH)_4^{2-}$, $Zn_2(OH)^{3+}$, $ZnNO^{3+}$ and $ZnOH^+$.

In 0.1 M citric acid, the desorption efficiency was higher than in 0.5 M citric acid solution. The speciation profile for these solutions showed presence of $Zn(C_6H_5O_7)_2^{4-}$ and $Zn(C_6H_5O_7)^-$ complexes; with their higher content in 0.5 M solution. It is suggested that the adsorption of Zn-citrate complexes dominated over desorption of zinc ions at pH 3.5 [13]. In addition, pH_{pzc} of PSAC was determined to be 9.2 [14], which implies a positive surface charge on PSAC surface at pH 5. It enhances the electrostatic interaction towards negatively charged zinc complexes, thus promoting adsorption instead of desorption.

As the initial zinc concentration increased from 10 to 100 ppm, the efficiency of zinc desorption also correspondingly increased in all desorption solutions. Among the three desorbing agents, hydrochloric acid showed better results and it was selected for subsequent zinc deposition experiments.

Cathodic reduction behaviour of zinc in desorption solutions

Reduction of zinc in 0.1 and 0.2 M HCl desorption solutions

Fig. 1(a) shows cyclic voltammograms for 10 ppm of Zn in 0.1 M HCl solution at a scan rate of 0.1 V/s and a range of different potentials. No reduction peak was observed at any of the tested potentials up to -1.45 V; however, an anodic peak was observed at around -0.10 V indicating the anodic dissolution of the earlier

electrodeposited zinc. In the desorption solution of zinc with added 0.25 M KNO_3 , a reduction peak appeared at the potential of -0.98 V. It was broad, probably due to the occurrence of hydrogen evolution. Further diminution of the current towards 0.0 V can be explained by the decrease in the electrolyte concentration within the diffusion layer around the cathode surface. During the reverse scan, hydrogen reduction slowed down significantly resulting in the gradual current drop. A crossover feature between forward and reverse scan was noticeable at a potential of -0.80 V, which is characteristic for the nucleation reaction [15]. However, no other distinctive peaks were observed throughout the reverse scan.

The observed zinc reduction potential was slightly higher compared to the zinc standard half-cell potential of -0.76 V, which is attributed to the use of a different metal electrode, stainless steel cathode. When pH buffer was added to the above desorption solution, containing biphthalate ions, $HC_8H_4O_4$, the zinc reduction potential became more negative, -1.22 V. The reduction peak was followed by a current plateau of about 15 mA current level indicating a mass transfer control process. One of the possible explanation for the increase in deposition potential is formation of a variety of coordination complexes such as $Zn(OH)^{3-}$, $Zn(OH)_4^{2-}$, $Zn(C_8H_4O_4)_2^{2-}$, $ZnCl_3^-$ and $ZnCl_4^{2-}$ suggested by the chemical speciation software VMinteq. The dissociation of these complexes would require higher reduction potential to release zinc cations from the negatively charged ligands [16]. The addition of pH buffer facilitates maintenance of the solution's pH at pH 4 level to counter pH changes occurring due to the hydrogen evolution reaction at the cathode. pH 4 was reported to yield 98.8 % of current efficiency [17] in the deposition of Zn-Ni-Fe alloy from a sulphate bath.

Fig. 1(b-c) shows CVs for the solutions of 50 and 100 ppm zinc concentration, respectively. The composition of the solutions was the same as above and the resulting electrochemical reduction behaviour of zinc was very similar as well. No reduction peak was observed in the solution with only zinc. A slightly sharper reduction peak was notable upon addition of KNO_3 . The increased concentration of zinc had effect on the reduction potential decrease, which was less negative, -0.86 V, as compared to -0.98 V in 10 ppm zinc solution. The addition of pH buffer to 50 ppm of zinc solution increased the reduction

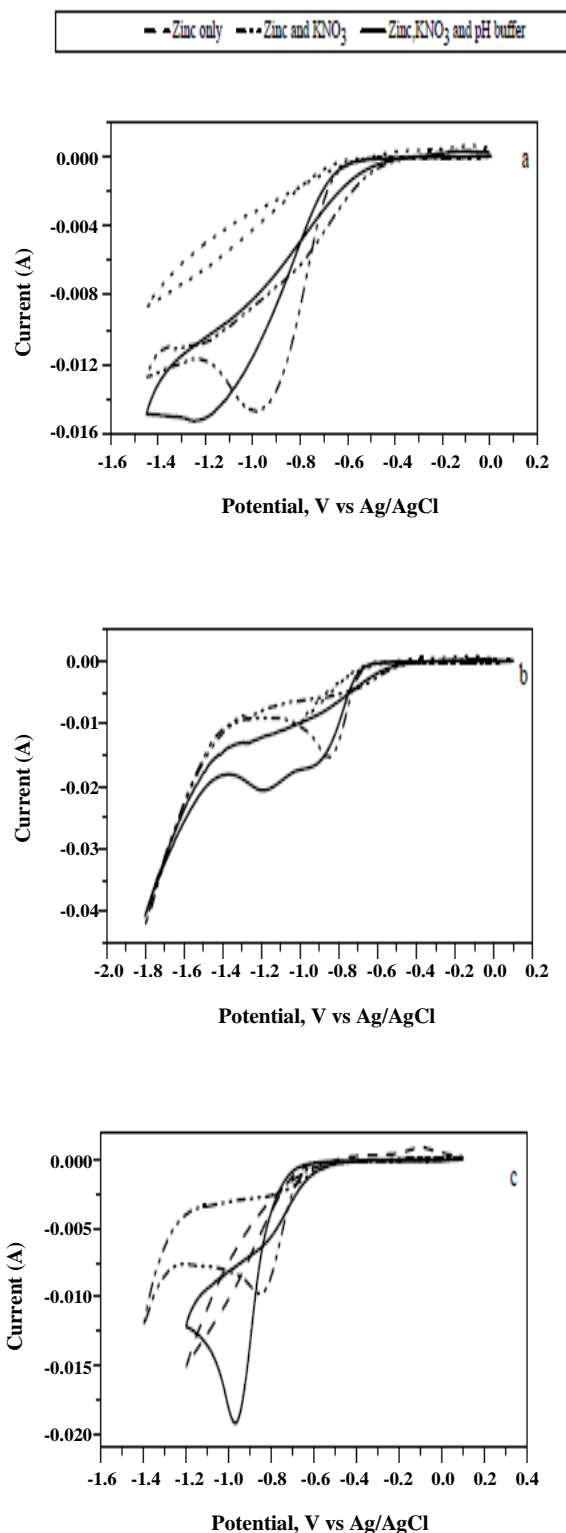


Fig. 1: Cyclic voltammograms for 0.1 M HCl with different concentrations of Zn: (a) 10 ppm (b) 50 ppm (c) 100 ppm.

potential to a more negative potential of -1.19 V as compared to 10 ppm zinc solution. In 100 ppm zinc solution with KNO_3 , the zinc reduction potential was very close to the one in 50 ppm zinc solution, -0.85 V. However, the reduction potential decreased to -0.97 V upon the addition of pH buffer. It can be noted that the increased zinc concentration in the above solutions was reflected in the lower zinc reduction potential. Such change is in line with the Nernst equation: the higher concentration of Zn^{2+} , the lesser applied voltage is required. The addition of pH buffer to the 50 and 100 ppm zinc solutions had a similar effect, zinc reduction potential decreased from -1.22 V in 10 ppm solution to -1.19 V in 50 ppm solution, and finally to -0.97 V in 100 ppm solution.

A higher cathodic current is noticeable in every CV in Fig. 1(a,b) as compared to 1(c). It decreased in 100 ppm zinc solution due to the slower hydrogen evolution reaction as fewer hydrogen gas bubbles were observed during these experiments. It was anticipated to obtain high zinc reduction as it requires less voltage compared to the hydrogen ions reduction.

Another possible explanation for the higher cathodic current is the shielding effect attributed to zinc ions of larger ionic radii covering the cathode surface. Since ionic radius for hydrogen and zinc ions are 0.012 Å and 0.74 Å, respectively [18], it was suggested [19] that cathodic current increases exponentially when hydrogen ions concentration increases. In addition, a very sharp reduction peak was observed in Fig. 1(c) as compared to (a) and (b) supporting the observation that hydrogen evolution phenomenon was minimal in the solution of the highest zinc concentration.

Reduction of zinc in 0.2 M HCl

Fig. 2(a) presents CVs obtained in 0.2 M HCl. Overall, all CVs exhibit similar features as discussed for Fig. 1(a). It was anticipated that the increase in acid concentration also amplifies the hydrogen evolution reaction. The adsorption of hydrogen ions on the stainless steel electrode surface enhances, thus reducing the active metal deposition area and enhancing the resistance between the bulk electrolyte and electrode. Once KNO_3 was added, a reduction peak appeared at the potential of -0.94 V, slightly higher as compared 0.1M HCl solution. It is attributed to the ratio of hydrogen ions to zinc ions that shifts to a less negative potential, in accord to Nernst

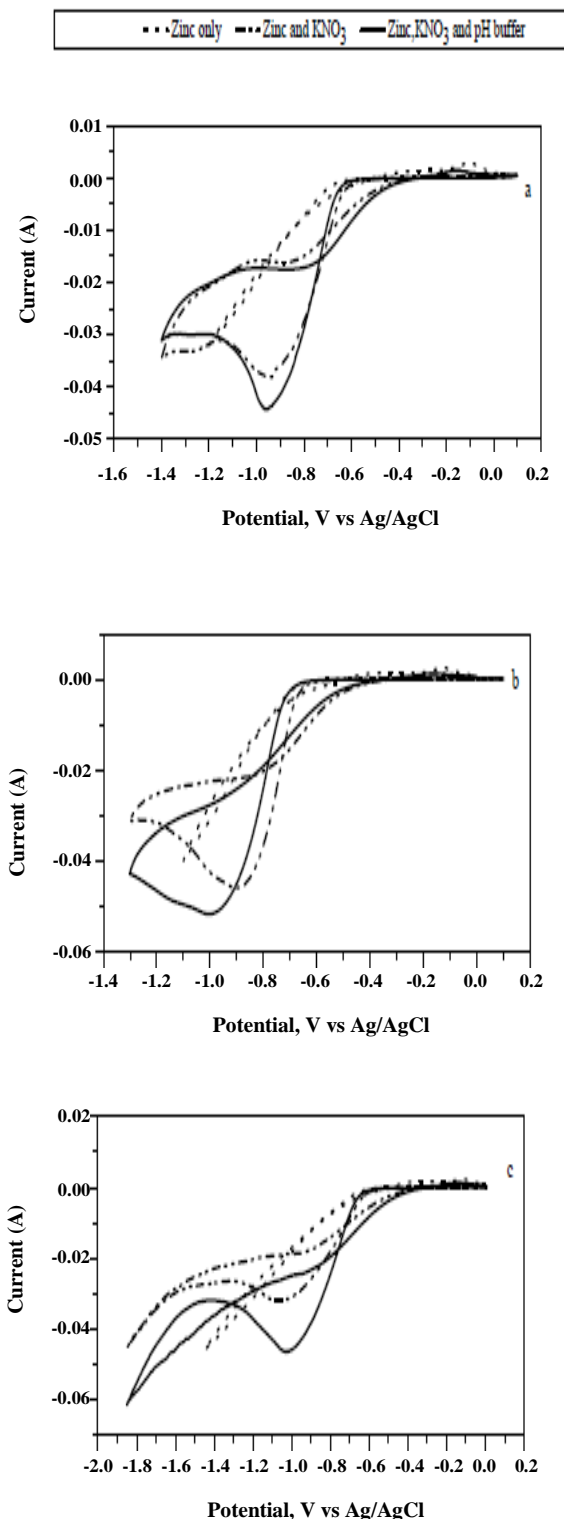


Fig. 2: Cyclic voltammograms for 0.2 M HCl with different concentrations of Zn: (a) 10 ppm (b) 50 ppm (c) 100 ppm.

equation [15,20]. The addition of pH buffer showed increase in the reduction potential to -0.95 V, which is significantly lower compared to -1.22 V in 0.1 M HCl. The reduction in the latter potentials shows that the increase in hydrogen ions concentration reduces zinc electrodeposition voltage [21].

Reduction of zinc in 0.1 and 0.2 M HNO₃ desorption solutions

Figs. 3 and 4 show the CVs obtained in 0.1 and 0.2 M HNO₃ solutions. Again, no reduction peak was observed in zinc only solutions of all concentrations. Cathodic peak potentials of -0.87 V and -1.05 V were observed in zinc solutions with KNO₃ and buffer agent, respectively. The reduction potentials were lower compared to the ones in HCl desorption solutions. Such changes can be explained by a stronger blocking effect caused by chloride ions as compared to nitrate ions [15,16]. Upon addition of pH buffer, the peak became broader in shape and the potential was more negative due to the formation of coordination complexes such as: Zn(OH)³⁻, Zn(OH)₄²⁻ and Zn(C₈H₄O₄)₂²⁻ as suggested by the Visual Minteq speciation profile. Higher reduction potential is needed to release positively charged zinc ions from the ligands due to the decline in the activity of free moving ions. Comparison between HCl and HNO₃ solutions indicated that the reduction potential in the presence of the buffer agent was lower in HNO₃ solution; it increased from -1.22 to -1.05 V. It is suggested that a fewer complexes are formed in the nitric acid solution than in the hydrochloric acid desorption solution. The effect of zinc concentration was similar as discussed for HCl solutions.

Fig. 4 also shows that increase in nitric acid concentration to 0.2 M resulted in a shift towards less negative cathodic potentials for solutions with KNO₃, from -0.87 to -0.85 V; and with buffer agent it increased from -1.05 to -0.87 V. Besides, cathodic reduction of nitrate to nitrite ions also occurred at a less negative potentials suppressing zinc reduction.

The voltammograms depict almost the same shape indicating that the process is diffusion controlled [22]. Besides, the reduction peak appeared to be sharper as compared to the previous peaks due to the nitrate ions reduction suppressing the hydrogen evolution. Similar trends can be observed in CVs shown in Fig. 4, whereby: (1) no reduction peak for solutions with zinc only;

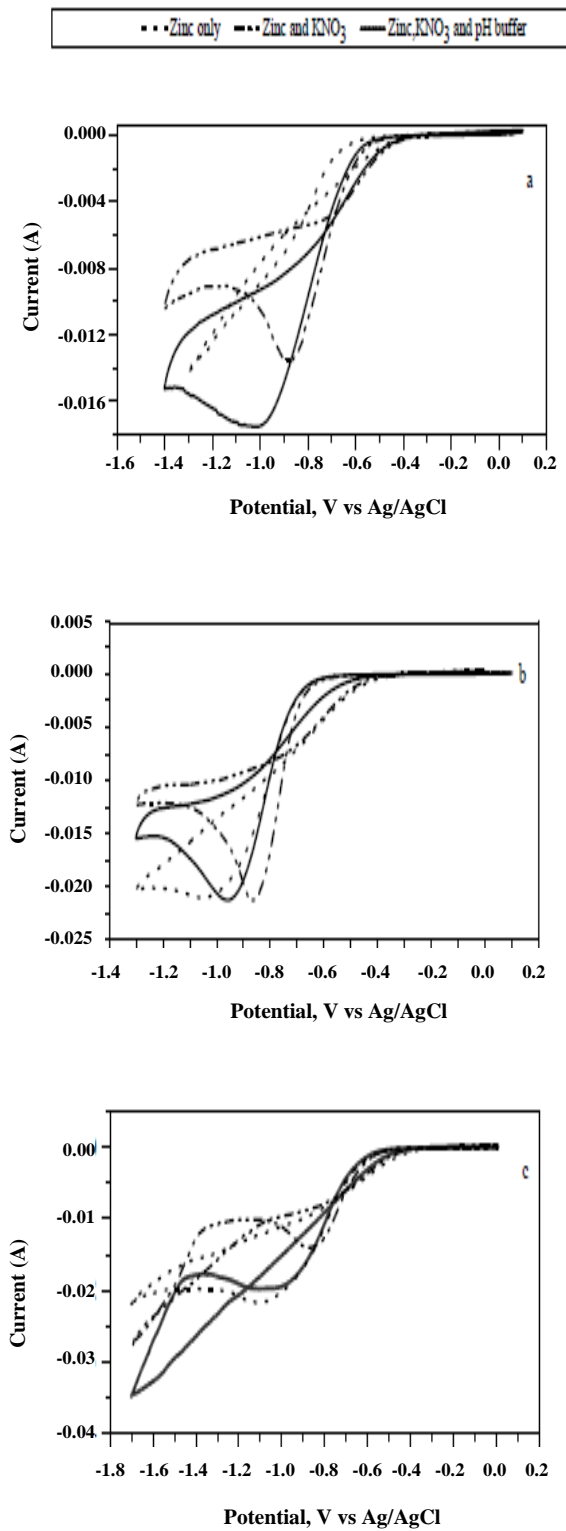


Fig. 3: Cyclic voltammograms for 0.1 M HNO_3 with different concentrations of Zn: (a) 10 ppm (b) 50 ppm (c) 100 ppm.

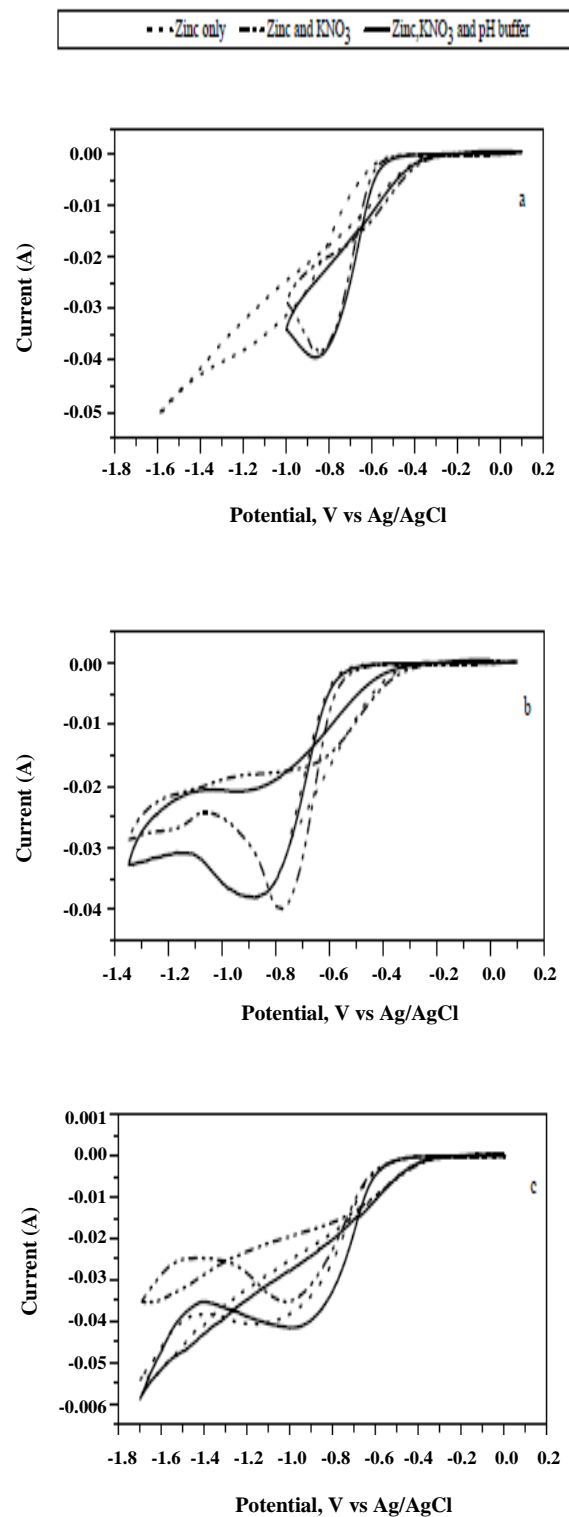


Fig. 4: Cyclic voltammograms for 0.2 M HNO_3 with different concentrations of Zn: (a) 10 ppm (b) 50 ppm (c) 100 ppm.

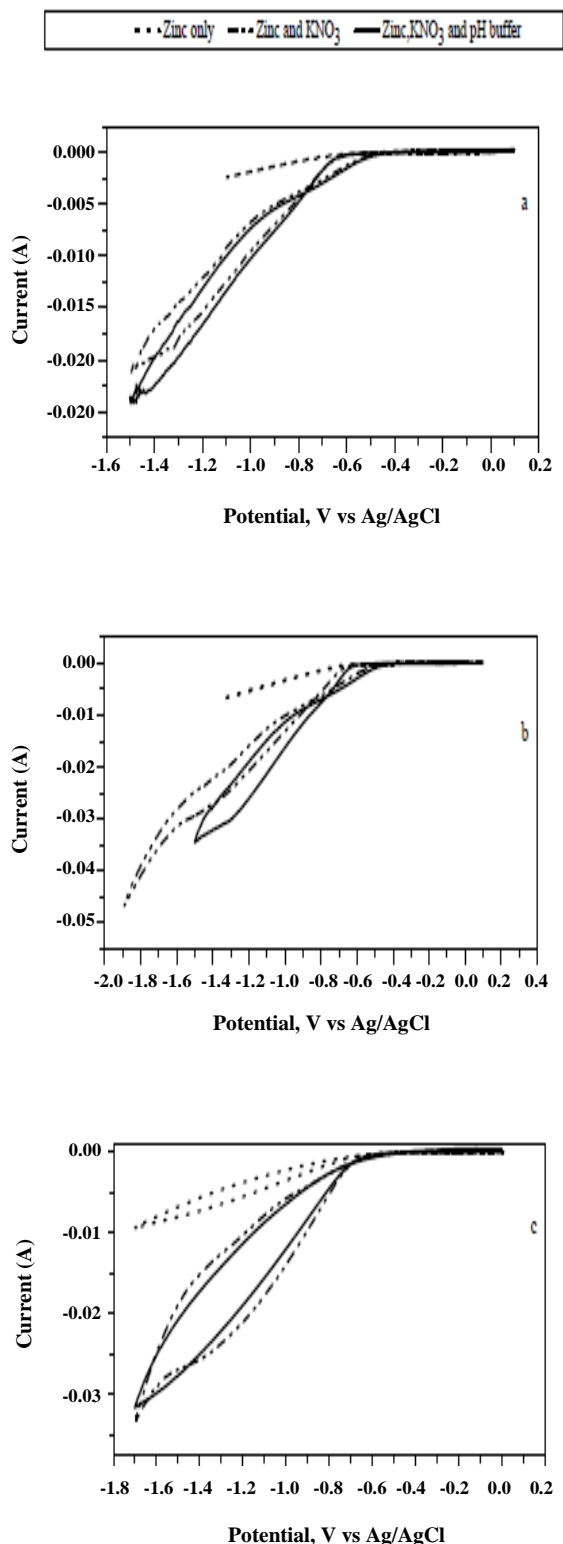


Fig. 5: Cyclic voltammograms for 0.2 M C₆H₈O₇ with different concentrations of Zn: (a) 10 ppm (b) 50 ppm (c) 100 ppm.

(2) reduction potential of zinc solutions with KNO₃ and added pH buffer increased to a less negative potential, and; (3) higher cathodic current suggesting more reactions taking place in the solutions.

Reduction of zinc in 0.2 and 0.5 M C₆H₈O₇ desorption solutions

Figs. 5 and 6 show the CVs obtained in 0.2 and 0.5 M citric acid desorption solutions. The electrochemical patterns observed in these CVs are very different as compared to hydrochloric and nitric acids. No zinc reduction peak was depicted in any of the solutions. Despite the absence of the reduction peaks, slight increase in the cathodic current was detected in the solution with KNO₃. The CVs suggest that citric acid is not a suitable supporting electrolyte to carry out zinc reduction as compared to HCl and HNO₃, mainly due to its tendency to form complexes with metals. A speciation profile by VMinteq suggested presence of the following species in the solution: Zn(C₆H₅O₇)₂⁴⁻, Zn(OH)³⁻, Zn(OH)₄²⁻, Zn(C₈H₄O₄)₂²⁻, Zn(C₆H₅O₇)⁻ and Zn₂OH₃. These complexes may occupy the electrode surface preventing release of zinc ions from the complexes and attraction of free zinc ions to the cathode surface [23]. As zinc concentration increased from 10 to 50 ppm and then to 100 ppm, the cathodic potential decreased; a similar trend was observed in HCl and HNO₃ solutions and it is associated with the decrease in the concentration overpotential, which facilitated the nucleation of Zn²⁺ ions on the cathode. Upon the increase of citric acid concentration from 0.2 M to 0.5 M, no noticeable changes were observed in all zinc solutions.

The speciation profile by VMinteq suggests that zinc ions have strong tendency to form complexes with citric acid and as the acid's concentration increased, more of such complexes are formed (e.g. ZnH₂Cit⁺, ZnH₂Cit and Zn(Cit)₂⁴⁻) thus dominating over the electroreduction of zinc [24,25]. Moreover, zinc citrate complexes occupy the cathode surface which in turn enhances the interfacial viscosity and decreases mass transfer from the bulk region; the subsequent increase of the potential showed no effect on the reduction of zinc.

Electrodeposition of zinc from desorption solutions

Table 1 presents desorption efficiencies obtained for the three desorption agents. The solution of 0.1 M HCl showed better performance in the desorption of zinc ions

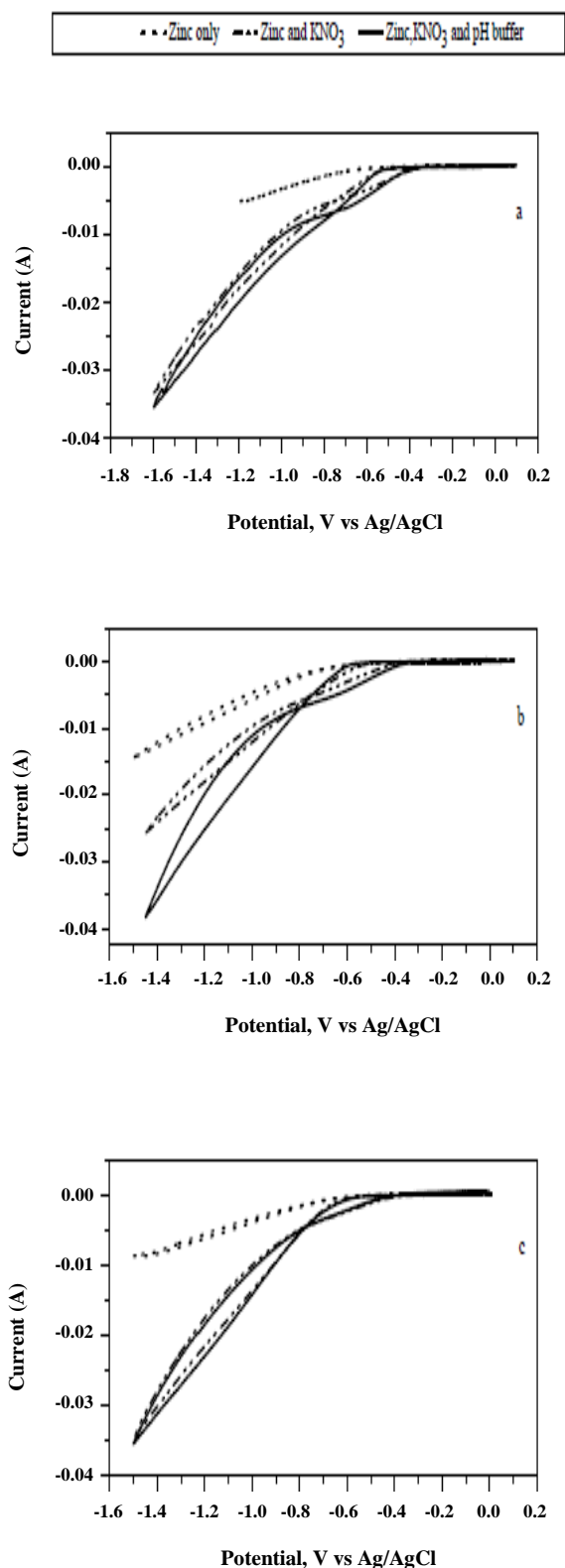


Fig. 6: Cyclic voltammograms for 0.5 M $C_6H_8O_7$ with different concentrations of Zn: (a) 10 ppm (b) 50 ppm (c) 100 ppm.

from the adsorbent surface as compared to the other two acids.

Table 2 shows zinc electrodeposition efficiency results for all desorption solutions used in CV tests. Again, 0.1 M hydrochloric acid solution showed better results as compared to the nitric and citric acids solutions.

Higher desorption and deposition efficiencies as well as the preferable zinc electroreduction behavior from the cyclic voltammetry results allowed selecting 0.1 M hydrochloric acid solution with KNO_3 and pH buffer as a suitable solution for zinc electrodeposition tests using chronoamperometry technique. Since an average concentration of zinc in the rubber manufacturing wastewater is 10 ppm, the solution of such concentration of zinc in 0.1 M HCl was subjected to the electrodeposition under the fixed current density of $100 A/m^2$ for 10 min. The resulting zinc concentration was 2.47 ppm, slightly above the permissible discharge limit of 2 ppm; when the electrodeposition duration was extended to 30 min, the final zinc concentration dropped by only 0.173 ppm. An attempt to increase the electrodeposition beyond 30 min showed visible changes in the test solution, it turned green colour indicating the release of nickel and chromium ions from the stainless steel electrode [26]. The measured concentration of these metals showed presence of nickel and chromium ions at 1.045 and 1.121 ppm levels, respectively. The increase in dissolution rate was obvious owing to the de-passivation of the stainless steel electrode surface initiated by the dissolution of oxide film and damage in the uniform surface layer [27]. Also, higher current density of $200 A/m^2$ was applied to 10 ppm zinc solution; however, the results showed very small increment in zinc deposition, from 64.3 to 65.8 %.

CONCLUSIONS

The results of cyclic voltammetry tests showed that zinc can be reduced in the desorbing solutions of hydrochloric and nitric acids. A noticeable improvement in the zinc reduction peaks appearance was observed at the presence of KNO_3 and buffer agent. Successful zinc electrodeposition was achieved in the 0.1 M HCl solution with KNO_3 and buffer agent, in which the initial zinc concentration of 10 ppm was reduced to 2.47 ppm within 10 min. The increase of the deposition duration and current density showed insignificant increment in the further zinc removal. Overall, this study demonstrated good feasibility

Table 1: Desorption efficiency of zinc in different desorbing agents solutions.

Desorbing agent	Acid concentration (M)	Desorption efficiency (%)		
		10 ppm	50 ppm	100 ppm
Hydrochloric acid	0.1	77.91	78.25	80.07
	0.2	71.59	72.00	73.71
Nitric acid	0.1	63.74	67.50	72.79
	0.2	69.39	72.45	75.00
Citric Acid	0.2	61.90	65.47	71.66
	0.5	47.26	56.39	58.61

Table 2: Deposition efficiency of zinc with different agents and concentrations.

Desorbing agent	Acid concentration (M)	Desorption efficiency (%)		
		10 ppm	50 ppm	100 ppm
Hydrochloric acid	0.1	64.33	65.62	71.34
	0.2	47.67	56.93	58.76
Nitric acid	0.1	48.32	59.37	59.41
	0.2	42.99	56.81	59.41
Citric Acid	0.2	33.81	43.70	50.08
	0.5	22.90	31.21	38.31

of the electrodeposition method application in the diluted zinc containing adsorption/desorption solutions, which can be used as a more effective alternative to the currently employed chemical precipitation treatment.

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