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# Investigation of Kenyan bentonite in adsorption of some heavy metals in aqueous systems using cyclic voltammetric techniques

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Potential application of Kenyan bentonite for adsorption of iron, cobalt, copper, nickel and zinc and for analysis of electroactive species in water from a polluted water course using a 3-electrode potentiostat and cyclic voltammetry was studied. Polished carbon graphite electrodes were used either bare or modified with Kenyan bentonite using an electrochemically inert adhesive to a thickness of about 0.8 mm. These were used to prepare calibration curves of iron, cobalt, copper, nickel and zinc by plotting cyclic voltammograms of the ions at different concentrations and using 0.1 M sulphuric acid as supporting electrolyte. The slopes of the curves from bentonite-modified electrodes were observed to be higher than those obtained from bare carbon electrodes by a factor of between 1.7 and 24, implying that bentonite enhanced electron transfer kinetics of the metal ions. It was also observed that the magnitude of the ratio depended on the proximity of the element to either filled or half-filled 3d orbitals, which implied that a chemical reaction may have taken place between the bentonite and the ions (chemisorption). Carbon graphite electrodes were modified with bentonite that had been soaked in water samples from a polluted water course at a ratio of 1:1 w/w. The cyclic voltammograms showed clear oxidative and reductive peaks indicating that electroactive species that previously could not be detected on the potentiostat were pre-concentrated on the bentonite and could thus be detected. Thus Kenyan bentonite is observed to chemically adsorb zinc, cobalt, copper, nickel and iron species in aqueous solution and can be used to monitor electroactive pollutants in aqueous systems using electroanalytical techniques.

**Key words:** Bentonite, heavy metals, surface modified electrodes, cyclic voltammetry, preconcentration, adsorption.

## INTRODUCTION

According to the Global Environment Assessment Report (UNEP/GEMS, 1991) in developing countries, untreated water is the most commonly-encountered health threat and causes about 25,000 deaths per day due to water-

borne diseases. Some of the pollutants that should be monitored regularly are heavy metals, as they have been known to be toxic especially when present in high levels (Normandin, 2004; Elbetieba and Al-Hammod, 1997;

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Tvrda et al., 2013; Lloyd, 1960; Pearce, 2007). Since water resources development and management contribute significantly to socio-economic development in Africa in general and to agricultural development in particular, there is an urgent need to monitor the level of these species in water.

Cyclic voltammetry is a versatile electro-analytical technique for the study of electro-active species, and has been labeled 'electrochemical spectroscopy' (Orata and Segor, 1999). Modified electrodes, that is, electrodes on whose surfaces that chemical species has been deliberately immobilized have been used to facilitate electron transfer from bacteria to electrodes (Heinze and Muller, 1998), as sensors (Guo et al., 2013; Rezaei et al., 2013), catalysts (Rahul et al., 2007) and to provide new methods of analysis (Nada et al., 2007; Kuralay et al., 2013; Oukil et al., 2007). Modified electrode surfaces can act as preconcentrating surfaces in which the analyte species is collected and concentrated on the electrode. The collected analyte is subsequently measured by the electrochemical response to a potential step or sweep.

Bentonite is a clay where the principal exchangeable cation is sodium. It has been used together with pure Bottom Ash (BA) as a land fill cover (Puma et al., 2013). It has also been used in modification of electrodes for various purposes, for example catalysis and photocatalysis (Li et al., 2013; Boz et al., 2013).

It has also been used to remove pollutants from waste waters (Jovic-Jovicic et al., 2013; Zhang et al., 2013; Shi et al., 2013; Reitzel et al., 2013). Kenyan bentonite has been used, with good results, to modify electrodes for electrodeposition of polyaniline (Orata and Segor, 1999). However, the same has not been used to monitor other species like cations in aqueous systems. In this project, electrodes modified using Kenyan bentonite were used to monitor adsorption and preconcentration of iron, nickel, copper, cobalt and zinc in aqueous systems. It was used to analyze electroactive species from a polluted water course could through electrochemical means. Cyclic voltammetry was used to monitor heavy metals in aqueous systems using Kenyan bentonite - modified electrodes.

## EXPERIMENTAL

All reagents used in the experiments were of analytical grade and were used without further purification. The water used to prepare the solutions was triply distilled and the experiments were performed in triplicate. The instruments used included a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, a logarithmic current converter model 396 that controlled the current, a PAR model 175 universal programmer and a PAR RE 0089 X-Y recorder. For the super dry conditions, a PAR model 362 scanning potentiostat/galvanostat and a Fluke and Philips PM 8271XYt recorder were used for electrochemical control and data recording respectively. Bentonite was obtained from Athi River Mining Co. Ltd., (Kenya) with a mesh size of 150 to 200  $\mu\text{m}$ ; a Cationic Exchange Capacity, CEC of 1.118 to 1.22 mM/g, a pH of 8.4 to 9.6

**Table 1.** Composition of bentonite.

Element	Concentration (mg/g)
K	8.350
Na	10.855
Ca	37.000
Mn	0.581
Fe	50.500
Al	171.100
Ni	0.016
Cu	0.069
Zn	0.096
Mg	16.500
Pb	0.021
V	0.124
Cr	0.068
Rb	0.069
Sr	0.313
Zr	0.142
Ti	8.100
Ba	3.776
SiO <sub>2</sub>	469.710
P <sub>2</sub> O <sub>5</sub>	0.569

and a density of 1.15 g/cm<sup>3</sup>. The elemental composition is shown in Table 1. The bare carbon graphite electrode of surface area of 0.38 cm<sup>2</sup> was polished on a felt polishing cloth containing alumina.

### Determination of type of reaction

To establish whether or not the reaction was diffusion –controlled, a 1,10 - phenanthroline complex of iron (BDH, England) was prepared by mixing 1 mg/L Fe<sup>2+</sup> solution with 3 mg/L 1,10 – Phenanthroline. The cyclic voltammetric response was recorded by scanning from -0.20V to + 0.85V at scan rates of 5, 10, 20, 50 and 100 mV/s using polished carbon graphite electrodes and 0.1 M H<sub>2</sub>SO<sub>4</sub> as supporting electrolyte. A plot of peak current versus the square root of the scan rate was plotted.

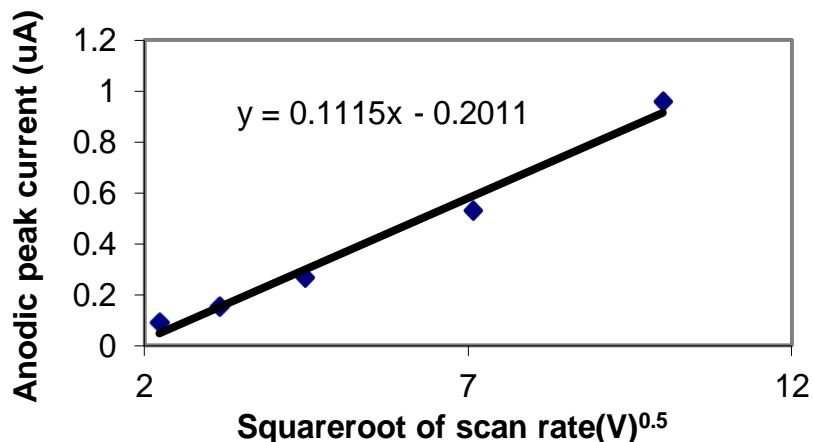
### Calibration curves

Calibration curves indicating variation of concentration with anodic peak current were plotted for both the non-modified and modified electrodes. 1000 mg/L stock solutions each of copper sulphate, cobaltous sulphate, zinc sulphate, nickel nitrate and ferrous sulphate all from BDH Chemicals were prepared. Lower concentrations ranging from 10 to 50 mg/L of each of the above solutions were obtained by appropriate dilution.

The bentonite-modified electrodes were formed using a slurry solution composed of 1 ml of an electrochemically inert adhesive from Henkel, Kenya with 0.1 g of bentonite. The mixture was spread on the surface of a polished carbon graphite electrode up to a thickness of about 0.8 mm and air-dried for 12 h. The surface area of the modified electrode was approximately 0.64 mm<sup>2</sup>. For non-modified electrodes, polished carbon graphite electrodes were used. For both working electrodes (modified and bare carbon), cyclic voltammograms of the different concentrations were obtained using the appropriate scan window depending on the oxidative (and

**Table 2.** Scanning potential range for various metal ions.

Metal ion	Cu	Zn	Ni	Fe	Co
Scan range (v)	-0.4- 0.75	-1.5 - 0.75	-0.2 - 0.75	-0.4 - 0.75	-0.2 - 0.75

**Figure 1.** Anodic peak current versus square root of scan rate for 1,10-phenanthroline – complex.

reductive) potentials observed for the metal ion (Table 2) at a scan rate of 10 mV/s. All the voltammograms were obtained after 5 min of equilibration.

#### Pre-soaking of bentonite on water samples

To investigate the ability of Kenyan bentonite to improve electron-transfer kinetics of the electro-active species in water samples, 50 g of bentonite was added to 50 ml of water from a polluted water course in Nairobi, Kenya. The mixture was continuously agitated for 24 h to ensure homogeneity. The slurry obtained was air-dried for 12 h and crushed to a homogeneous powder. The powder was used to modify electrodes and cyclic voltammograms obtained, using 0.1 M sulphuric acid as supporting electrolyte, from -1.5V to +0.8V.

## RESULTS AND DISCUSSION

### Investigation of the nature of reaction

In the study to determine the nature of reaction of the metal ion at the surface of the bare carbon electrode with 1, 10-phenanthroline – Fe complex, it was observed that the peak current was linear to the square root of scan rate implying that the process was diffusion controlled as per the Cottrell equation (Cottrell, 1903) (Figure 1).

### Calibration curves: Comparison between modified and non-modified electrodes

Cyclic voltammograms obtained for Fe ions using both

the non-modified and modified electrodes are shown in Figure 2. The voltammograms for the modified electrodes looked slightly different from those of the modified electrodes and some of them had different oxidation/reduction peaks (Table 3). This could be attributed to the fact that bentonite is a carrier of electroactive species as part of its elemental composition (Table 1), and also the pH of the bentonite (8.4 – 9.6) may cause a change in the potential of the peaks, since pH generally affects adsorption and catalysis (Jovic-Jovicic et al., 2013; Soetaredjo et al., 2011). pH is also known to affect the stability of various species of elements (Millero, 2001). This may explain the different (predominant) peaks in the ions observed. Copper, for example has the predominant peak at a potential of 0.025 mV vs CE on bare carbon (pH of solution about 6) while at higher pH (pH of bentonite, 8.4 – 9.6) the predominant species is observed to have a potential of about 0.40 mV vs CE.

Another example is zinc, whose predominant species is observed to have a potential of -0.998 mV vs CE at neutral pH, while in the presence of bentonite (higher pH) the predominant species is observed to have a much higher potential of -0.143 mV vs CE. The other metal ions studied also showed some variation, which could likewise be attributed to a pH change. It may also have been due to interaction of the ions with the elements which make up the structure of bentonite (Table 1). Straight line calibration curves were obtained for all the metal ions studied. Some of the curves are indicated in Figure 3. The constants (slopes) for the calibration curves for the various metal ions are shown in Table 4.

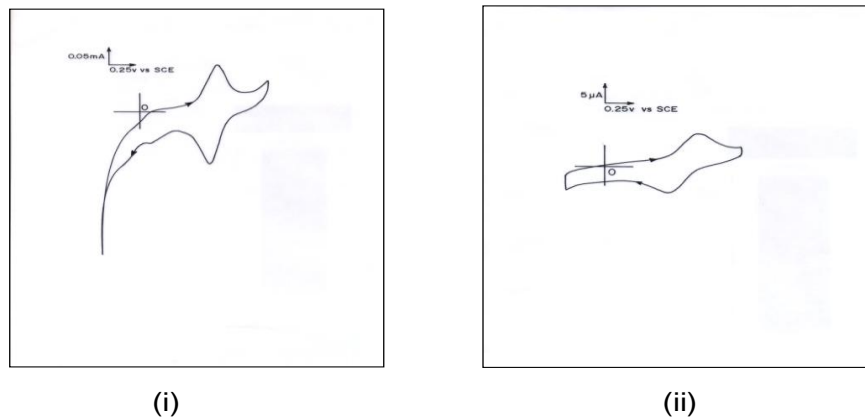


Figure 2. Cyclic voltammogram for Fe for unmodified (i) and modified (ii) electrodes.

Table 3. Anodic peak potentials of the metal ions  $E_p$  = of the non-modified electrode;  $E_p$  (CME) = of the modified electrode.

Metal ion	Cu	Zn	Ni	Fe	Co
$E_p$ (V)	$(0.025 \pm 0.001)^*$	$-0.998 \pm 0.020$	$0.450 \pm 0.025$	$0.420 \pm 0.032$	$0.590 \pm 0.071$
$E_p$ (CME)(V)	$(0.462 \pm 0.010)^*$	$-0.143 \pm 0.035$	$0.464 \pm 0.040$	$0.414 \pm 0.089$	$0.386 \pm 0.009$

\* A number of peaks were observed. The largest peak was used to obtain the calibration curve.

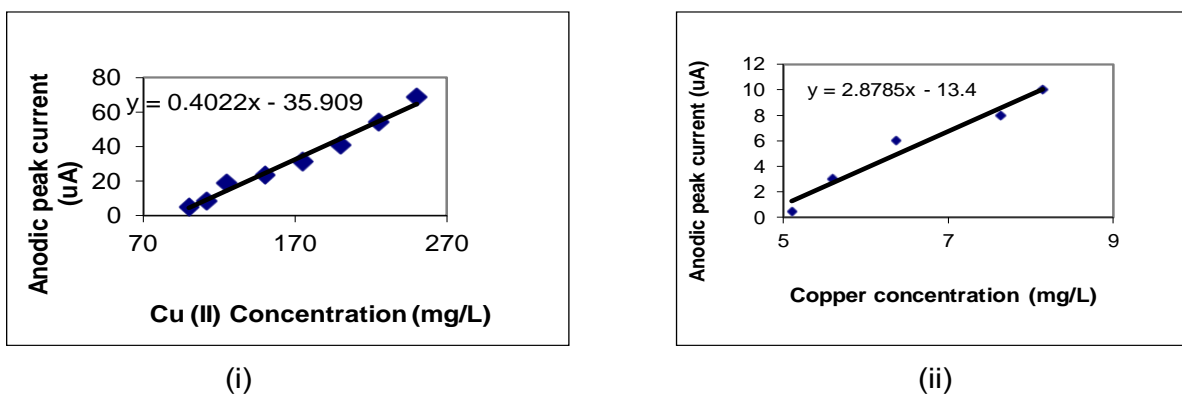


Figure 3a. Peak current vs copper concentration for (i) unmodified and (ii) modified electrodes.

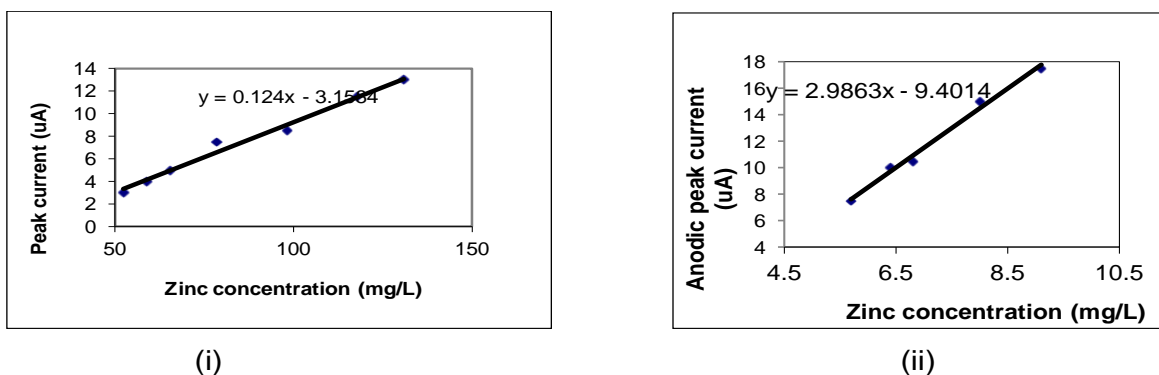


Figure 3b. Peak current versus zinc concentration for (i) unmodified and (ii) modified electrodes.

**Table 4.** Values for slopes obtained in calibration curves for bare carbon and for the modified electrodes.

Slope( $\mu\text{A}/\text{mg/L}$ )	Cu	Zn	Ni	Fe	Co
Slope (bare C)	0.402	0.124	0.413	0.905	0.023
Slope (CME)	2.878	2.986	0.736	6.67	0.196
Ratio: CME/bare C*	7.159	24.081	1.782	7.370	8.521

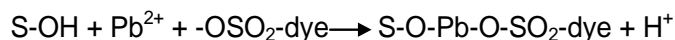
\* No units.

**Table 5.** Some peaks observed for the samples from Water samples preconcentrated on bentonite.

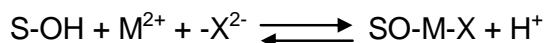
Site number	Anodic peak voltage vs SCE(v) ( $\pm 0.001$ )
1	-0.498, -0.114, 0.057, 0.100, 0.192, 0.541, 0.584, 0.683
2	-0.484, -0.107, 0.029, 0.085, 0.256, 0.355, 0.427, 0.470
3	-0.455, 0.0285, 0.071, 0.114, 0.182, 0.455, 0.541
4	-0.498, -0.128, 0.114, 0.142, 0.413, 0.463.
5	-0.484, -0.228, 0.085, 0.128, 0.185, 0.227, 0.389, 0.427.
6	-0.455, -0.313, -0.128, 0, 0.043, 0.085, 0.128, 0.399, 0.455.

It is observed that the CME/bare carbon ratio is greater than one in all the metal ions investigated, indicating that the concentration of the analyte is higher in the bentonite matrix than in solution, a factor that indicates that bentonite enhances the electron transfer kinetics of the metal ions investigated (Orata and Segor, 1999). This may indicate that there is preconcentration of electroactive species due to the presence of bentonite by factors ranging from 1.782 for nickel to 24.081 for zinc.

It is observed that the more stable the element (the higher the proximity to the stable  $3d^5$  or  $3d^{10}$  configuration), the higher the ratio between the modified electrode and the bare carbon electrode. An observation which implied that the difference in analyte preconcentration depends on the stability of the metal ion in the periodic table, which may in turn indicate that a chemical reaction takes place between bentonite and the metal ion in question. The mechanism followed by this adsorption may be one proposed by Jovic-Jovicic et al. (2013) and Ma et al. (2011) when they observed adsorption of  $\text{Pb}^{2+}$  on bentonite. Most probably the adsorption of the cations follow two mechanisms: cation exchange with inter-layer exchangeable cations and bonding to the silanol or alumino groups at the edge smectite. Jovic-Jovicic et al. (2010a) propose that the molecules they were investigating (RB5) could be adsorbed due to electrostatic interaction of  $-\text{SO}_3^-$  groups from the dye with previously adsorbed  $\text{Pb}^{2+}$  ions at the edge sites. The reaction they proposed is as follows:



The same reaction is proposed in the cations involved in the Kenyan bentonite.



Where  $\text{M}^{2+}$  is the metal ion,  $\text{X}^{2-}$  is the anion in solution and S is the bentonite surface. It is therefore expected that adsorption would be pH-dependent, given that a hydrogen ion is removed as a by-product. This may explain the shift in anodic peak potential for some ions when adsorbed on bentonite.

### Preconcentration with water samples

Further experiments were performed to investigate preconcentration of electroactive species from samples of water obtained from sampling sites on a polluted water course in Nairobi, Kenya on bentonite. Some of the peaks observed for each sampling point are given in Table 5. Most aqueous systems contain relatively low concentration of metal ions which may not be detected on a potentiostat, and preconcentration may be necessary in order to elicit a response. It is clear that if bentonite did not adsorb/ preconcentrate [electroactive] species there would be no observable response from the potentiostat. However, for all the bentonite electrodes that had been pre-soaked in the water, clear peaks were obtained (Table 5). These results corroborate those observed by Orata and Segor (1999). Thus bentonite-modified electrodes can be used to monitor pollution levels in, for example, aqueous systems.

### CONCLUSION AND RECOMMENDATIONS

Kenyan bentonite was investigated for adsorption and

preconcentration of metal ions. Straight line calibration curves were obtained with bentonite-modified electrodes with slopes of between 0.196 and 2.986  $\mu\text{A}/\text{mg}/\text{L}$ . The slopes of the curves of modified electrodes were higher than those of non-modified electrodes by a factor of between 1.7 and 24 which means that bentonite adsorbed and preconcentrated the metal ions. It was also observed that the magnitude of the ratio depended on the proximity of the ion being investigated to the stable 3d configuration (either filled or half-filled 3d orbitals). This may mean that chemical rather than physical adsorption took place. When electrodes were modified with bentonite that had been soaked with water samples from a polluted water course, the response indicated that the electroactive species in the water could be detected on a potentiostat. Thus Kenyan bentonite can be used in analysis of species in aqueous solution through preconcentrating the species on the bentonite. Spiking can be used to identify the species observed on preconcentration on water samples on bentonite. It is also recommended that other methods (eg. computational speciation programs) be used to compare the species observed electrochemically with those suggested by such programs.

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## Conflict of Interest

The author(s) have not declared any conflict of interests.

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