ASSESSING THE EFFICIENCY OF ELECTROCHEMICAL TREATMENT IN REMOVING SELECTED POLLUTANTS FROM GOLDMINE WASTEWATER IN ITAGUNMODI, OSUN STATE, NIGERIA

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Abstract

The study examined some physical and chemical characteristics of wastewater in an unmonitored mining community (Itagunmodi) in Osun State, Southwestern Nigeria. This study aims at investigating the ability of electrochemical treatment method to remove selected contaminants from the wastewater emanating from these gold mining sites, with a view to reclaiming this scarce resource for other uses without any toxic effect on man and animals. Wastewater samples were collected twice in a month from four main ponds in October (rainy season) and February (dry season) making a total of sixteen (16) wastewater samples. The wastewaters collected were characterized (turbidity, solids, chloride, pH) using standard procedures; subjected to electrochemical treatment at laboratory scales and effects of selected factors (operating time, stirring speed, contact area to volume ratio and pH value) on the performance of the electrochemical treatment were evaluated using orthogonal array factorial experiment (4^4). Performance of the electrochemical treatment of the wastewater was based on the ability to reduce selected parameters. The treatment showed that the process was capable of removing 70.42% of turbidity, removed 99.69% of suspended solid and removed 80.72% of total solids concentration. It also revealed that the selected factors had effects on contaminants removal. The study concluded that electrochemical method is a viable method in removing physico-chemical contaminants without losing much of the electrodes.

Keywords: electrochemical treatment, turbidity, pH, solids, wastewater, 4^4 orthogonal array factorial

Introduction

Most industrial processes and mining in particular produce significant environmental pollution. As a result, there is a growing concern about the quality of the living environment which calls for more innovative efforts to protect the environment. Now, the industries are expected to pro-actively reduce the amount of pollutants discharged into the environment. Mining affects fresh water through heavy use of water in processing ore and major water pollution results from discharged mine effluent, seepage from tailings and waste rock impoundments. Surface gold mining operations basically involves the clearing of vegetation cover from the area to be mined, striping off topsoil, creating pit with ramps, waste rock dumps and / or stock piles and haul roads. Gold extraction process depends on the ore mineralogy of the area being mined. However, if its activities are not well monitored and proper measures put in place, it will be a major cause of environmental degradation (e.g. loss of farm land, air pollution, water resource contamination etc.). It is thus essential to identify the water sources within the gold mining area and determine the actual sources of impact on the quality of water in relation to the geochemistry or mining activity. Singh *et al.*, (2005) considered rivers among the most vulnerable water bodies to pollution which necessitates the prevention and control of the pollution of these resources to have reliable information on the quality of the water. Human activities such as population growth and his quest for survival, elevated living standards, excessive exploitations of groundwater and climate changes, depends largely on clean water availability and supply, which impresses the need to find alternative water sources in cases of water contamination (Kalavrouziotis *et al.,* 2013). Mining by its nature consumes, diverts and can seriously pollute water resources. Negative impacts can vary from the sedimentation caused by poorly built roads during exploration through to the sediment, and disturbance of water during mine construction. The consequences of improper management of this water culminate in different life threatening water-borne diseases. Studies have also indicated that mine sites are around farmlands where chemicals may accumulate in fruits and leaves of arable and cash crops, and that soil contamination in mine sites can cause severe heavy metal contamination of water sources and poisoning of humans and animals, if ingested (Bartrem *et al*., 2014; Lo *et al*., 2012; Oramah *et al*., 2015; Plumlee *et al*., 2013). Poisoning by materials associated with mining has been associated with increased cases of kidney pain, respiratory problems, dizziness, and miscarriages in women, and deaths in many residents of communities where mining activities are carried out (Twerefou *et al*., 2015). The impacts of these contaminants depend on a variety of factors such as the sensitivity of local terrain, the composition of minerals being mined, the type of technology employed, the skill, knowledge and environmental commitment of the company, and finally, ability to monitor and enforce compliance with environmental regulations.

The contaminants have to be removed from the water sources in an efficient and economical way to enable consumers live a healthy live. The study seeks to assess and compare the physico-chemical qualities of water sources in Itagunmodi and its environs in order to attempt removing the contaminants. Previous researchers who attempted to remove these toxic contaminants from wastewater used Chemical methods, but the current cost of chemicals and availability of the required chemicals makes the method a little cumbersome, hence the need to remove these toxic contaminants through electrochemical method.

Materials and methods

Itagunmodi, is located within 7°30′N–7°36′N and 4°37′E–4°42′E, in the southwest Nigeria. The climate is characterized by tropical wet and dry climate in the rainforest ecological region. Mean annual temperature varies between 26°C and 28°C, while relative humidity over the area varies from 60 to 80%. Average rainfall is about 140 cm per year. The geology is characterized by Amphibolites rocks, and the soils belong to the Itagunmodi Association of the southwest Nigeria (Smyth & Montgomery, 1962). In terms of the human geography, Itagunmodi is a typical rural area with high records of migrants that work on the mine fields. A cursory interaction with the workers at about two major sites revealed that about 80% are migrants from the northern region of the country. The migrant workers have, however, been settled (mostly temporarily) in the area. The residents depend largely on the two streams connecting the community for their source of water which is largely polluted by the influence of the industrial activity in and around the community. Previous researchers who attempted the removal of these toxic contaminants from wastewater used chemical methods, but the current cost of chemicals and availability of the required chemicals stalled the process, hence the need to remove these toxic contaminants through electrochemical method.

The main materials used were the electrolysing unit (convert alternating current to direct current), electrodes (carry the currents in and out of the wastewater) and alternating current source. Electrolysing equipment was used to convert alternating current to direct current with a fixed voltage of 20 DC volts. The electrodes used were aluminium electrodes (cathode and anode). The electrodes were selected based on literature such as Chen (2004); Akintomide (2008), Oke (2006), Oke (2012a and b). The sites were visited and the discharge points of this wastewater were carefully studied. Two main ponds were located in each of the sites taking its recharge from wastewaters from processing points (smaller ponds). The main pond which receives fresh wastewaters overspills and discharges into the receiving streams leaving others at the abandoned sites. Wastewater samples were collected from these two main ponds twice during the rainy and dry seasons making a total of eight (8) samples, to assess the impact of seasonal variations on the wastewater. The wastewater samples were characterized for initial concentration of contaminants using standard methods. Electrolysing equipment was calibrated with a standardised voltmeter. Effects of input voltages and currents on the performance of the equipment were studied and evaluated using one-way analysis of variance (ANOVA). The collected wastewater samples were subjected to electrochemical treatment in accordance with orthogonal factorial experiment design. Table 3.1 shows the arrangement of the selected factors (operating time, stirring speed, pH and contact area to volume ratio) during the electrochemical treatment process. The arrangements and the levels of the factors were based on previous studies such as Akintomide (2008), Oke (2006 and 2009).

Table 3.1: The factors and the levels of the experimental design method for the electrochemical treatment process of the selected wastewater

Experiment	Code (level) Time	Ss	Cv	pH	Values for the codes Time (min.)	Ss (Rev/ min)	Cv (cm^2/cm^3)	pH
1	1	1	1	1	20	100	0.17	4.50
2	1	2	2	2	20	130	0.20	5.50
3	1	3	3	3	20	170	0.25	7.50
4	1	4	4	4	20	200	0.33	8.50
5	2	1	3	2	30	100	0.25	5.50
6	2	2	4	1	30	130	0.33	4.50
7	2	3	1	4	30	170	0.17	8.50
8	2	4	2	3	30	200	0.20	7.50
9	3	1	4	3	40	100	0.33	7.50
10	3	2	3	4	40	130	0.25	8.50
11	3	3	2	1	40	170	0.20	4.50
12	3	4	1	2	40	200	0.17	5.50
13	4	1	2	4	50	100	0.20	8.50
14	4	2	1	3	50	130	0.17	7.50
15	4	3	4	2	50	170	0.33	5.50
16	4	4	3	1	50	200	0.25	4.50

Efficiency of the process was based on ability to remove selected physico-chemical pollutants (turbidity, chloride, pH, suspended solids and total solids). The electrodes used during the electrochemical treatment were aluminium electrodes (cathode and anode) which were selected based on previous studies (Panizza *et al*., 2001), (Lo *et al*., 2004), (Akintomide 2008), (Oke 2006), (Oke 2009), The distance between the two electrodes and the voltage supplied were kept constant based on literatures (Oke 2006 and 2007), (Akintomide 2008). The standard method used in the determination of effects of the factors was based on statistical methods. The formulas and equations utilized in establishing the effects of the factors on electrochemical treatment are as follows;

K1= Summation of percentage pollutant removed for factor in level 1
K2= Summation of percentage pollutant removed for factor in level 2
K3= Summation of percentage pollutant removed for factor in level 3
K4= Summation of percentage pollutant removed for factor in level 4

Sum of Average of factors (SAF) = $\sum_{i=1}^{16} Average_i$ (3.1)

Sum of square of Average factors (SSAF) = $\sum_{i=1}^{16} Average^2{}_i$ (3.2)

Constant (C) = $SAF^2 / 16$ (3.3)

Sum of Factors (SF) = $\sum_{i=1}^{4} K^2{}_i / 4$ (3.4)

Sum of Squares (SS) = SF – C (3.5)
Total of Factors (TC) = SSAF – C (3.6)

Error = TC - $\sum_{i=1}^{4} K_i$ (3.7)

Mean Sum of Squares (MSS) = SS/DF (3.8)
DF = Degree of freedom

Results and Discussion:
The results of the treatment process are presented under the following considerations (calibration of electrolyzing equipment, characterization of the wastewaters, treatment of the wastewaters, effects and optimization of the selected factors).

Calibration of Electrolyzing Equipment
The equipment was calibrated using a voltmeter. Results of the calibration are as presented in Tables (4.1a) and (4.1b). Table (4.1a) showed that there was a relationship between the expected and obtained voltages. The differences might be attributed to the lower voltage supply of electricity and its irregularity. In the same vein, Figures (4.1a) and (4.1b) revealed that a relationship between the expected and obtained current could be established. Table (4.1c) presents the result of the analysis of variance (ANOVA) for the calibration of the equipment based on voltage; this revealed that there is no significant difference between the outputs (expected and obtained voltages). The F-values and probability values were 0.00 and 0.98 respectively ($f_{1,8}$ =0.00; p=0.98, P > 0.05) at 95% confidence. Table 4.1d shows the result of the Analysis of variance (ANOVA) for the calibration of the equipment based on current. The result revealed that there was no significant difference between the outputs (expected and obtained currents). The F-values and probability values are 4.96 and 0.99 ($f_{1,10}$ =4.96; p=0.99, p > 0.05) which confirms that there were no significant differences between the outputs (expected and obtained) at 95% confidence level.

Table 4.1a: Calibration of Electrolysing Unit (Voltage)

Expected Voltage (V)	Obtained Voltage (V)
0	0.18
5	4.88
10	9.76
15	14.92
20	19.75

Table 4.1b: Calibration of Electrolysing Unit (Current)

Expected Current (A)	Obtained Current (A)
0	0.02
2	2.20
4	3.98
6	5.94
8	7.90

Table 4.1c: Analysis of variance (ANOVA) of the calibration of equipment (Voltage)

Source of Variation	Sum of Squares	Degree of freedom	Mean of Squares	F	P-value	F-critical
Between the experiment.	0.02	1	0.02	0.00	0.98	5.31
Within the Voltage	491.92	8	61.49			
Total	491.94	9				

Table 4.1d: Analysis of variance (ANOVA) of the calibration of equipment (Current)

Source of Variation	Sum of Squares	Degree of freedom	Mean of Squares	F	P-value	F-critical
Between the experiment.	3.33×10^{-5}	1	3.33×10^{-5}	2.42×10^{-6}	0.99	4.96
Within the Current	137.77	10	13.77			
Total	137.77	11				

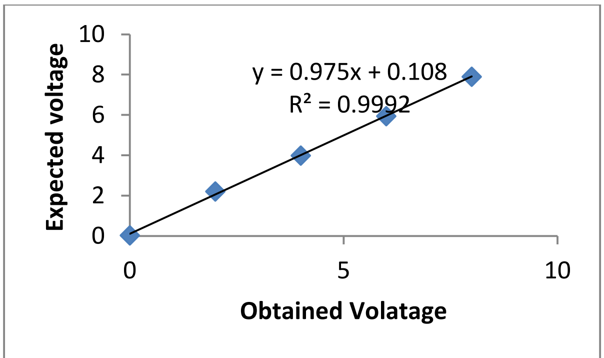

Figure 4.1a: Relationship between expected and obtained voltages in the calibration of equipment

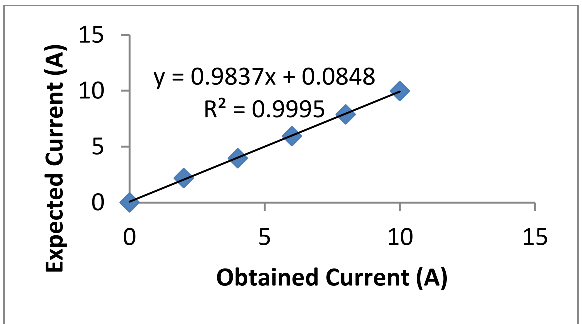

Figure 4.1b Calibration of Electrolysing Unit (current)

Characteristics of the Selected Wastewater.

Table 4.2 presents the result of the average measurements of initial concentration of various contaminants in the wastewater.

Turbidity: This is known as the measure of light intensity of a wastewater. From the Table 4.2, the turbidity of the wastewater samples at the different locations are between 92.51 and 95.42 NTU which indicates that the wastewater from the gold mining sites are turbid. The turbidity is high because the wet process involves washing of clay from the raw material which gives a high colloidal particle wash into the stream. Acheampong *et al.*, (2013) reported that wastewater from gold mining sites are naturally turbid, contains suspended solid and Total solids. Analysis of variance for the turbidity of the wastewater samples from the pond is given in Table 4.2a. The F-values and probability values are 7457.061 and 1.62x10^{-10} respectively ($f_{1,6}$ =7457.06; p=1.62x 10^{-10}, $p < 0.05$) at 95% confidence level. From the given values of f and p, there was a significant difference between the turbidity of the four sample points which is consequent to the fact that the bond in the colloidal particles would have been destroyed in the process of washing the clay.

Chloride: The wastewaters from the ponds have 4.998mg/l each. This is indicating that the levels of chloride ion contamination from these gold mining sites are minimal. FEPA (1991) provided a maximum limit of 600 mg/l of chloride for wastewater to be discharged into the environment. Acheampong *et al.*, (2013) reported that wastewater from gold mining sites may have minimal chloride. This is a factor of its high conductivity and higher percentage of total solids and ammonium. It therefore may not necessarily have chloride ions dissolved in it. Since the pond wastewater samples have equal amount of chloride concentration, it therefore suggests that it is impossible to have a significant difference in chloride concentration.

Table 4.2: Characteristics of the selected wastewater

Sample	1	2	3	4	5	6	7	8
Turbidity (NTU)	92.51	92.51	92.51	92.51	95.42	95.42	95.42	95.42
Chloride (mg/l)	4.99	4.99	4.99	4.99	4.99	4.99	4.99	4.99
Suspended Solids (mg/l)	1.05	1.05	1.05	1.05	1.02	1.02	1.02	1.02
Total Solid (mg/l)	0.06	0.06	0.06	0.06	0.07	0.07	0.07	0.07
pH	7.6	7.6	7.6	7.6	7.8	7.8	7.8	7.8

Table 4.2a: Analysis of Variance for the turbidity of wastewater samples from the pond.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2093.947	15	139.5964	7457.061	1.627E-10	1.894875
Columns	910.3061	3	303.4354	7457.061	1.627E-10	2.811544
Error	1308.668	45	29.08152			
Total	4312.921	63				

Table 4.2b: Analysis of Variance for the suspended solids of wastewater samples from the pond.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2093.947	15	139.5964	5.15	0.063422	3.6975
Columns	910.3061	3	303.4354	5.15	0.063422	5.9811
Error	1308.668	45	29.08152			
Total	4312.921	63				

***Suspended Solids*:** Table 4.2 shows that the wastewater samples from the ponds have appreciable suspended solids. It therefore becomes imperative to consider the removal of these suspended solids in our quest to improving the quality of the wastewater and removing hazardous contaminants from the wastewater. Viessman and Hammer (1993) reported that suspended solids deposition will impair the normal aquatic life of the receiving stream. Table 4.2b gives the analysis of variance (ANOVA) of the suspended solids with the F-value as 5.15 and the p-value to be 0.06 ($f_{1,6}$ =5.98; p= 0.06, p > 0.05). This analysis revealed that there is no significant difference between the suspended solids in the four sample points at 95% confidence level.

Total Solids: Table 4.2 shows that the total solid present as contaminants within the wastewater is ambiguous. This is so because; the wet process involves washing of clay materials from the raw materials into the stream. The wastewater is even cloudy at the point of obtaining the samples. Acheampong *et al.*, (2013) gave an impression that water from tale mines which eventually forms its wastewater must possess a considerable amount of total solids. Analysis of variance (ANOVA) of the total solid in table 4.2c revealed that the F-value is 446.43 and the p-value is $7.73x10^{-7}$ ($f_{1,6}$ = 5.15; p= $7.73x10^{-7}$, p < 0.05) which confirms that the P-value is less than the standard 0.05 which shows that there is a significant difference in the total solids of the wastewaters from the four ponds at 95% confidence level.

pH: This is the degree of acidity or alkalinity of the wastewater. The initial pH of the wastewater as obtained from the four ponds is as shown in the Table 4.2. This showed that the wastewater is basic. The wastewater has a pH value ranging between 7.6 and 7.8.

Table 4.2c: Analysis of Variance for the total solids of wastewater samples from the pond.

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Rows	2093.947	15	139.5964	5.15	7.73E-7	1.007973
Columns	910.3061	3	303.4354	5.15	7.73E-7	3.006701
Error	1308.668	45	29.08152			
Total	4312.921	63				

Electrochemical Treatment of the Wastewater

Removal of Turbidity from the wastewater: 4^4

Orthogonal factorial experiment was used in the selection and interaction of factors in the electrochemical treatment method. Table 4.3a presents the results of percentage removal of turbidity from the wastewater. The result showed that the process is capable of removing 42.42% of the turbidity contained in the wastewater. It further revealed that the combination that gives the optimum removal tendency is at a time 50 mins, stirring speed of 100 rev/sec, contact area to volume ratio of 0.20cm^2/cm^3 and pH of 8.50.

Removal of Suspended Solid from the wastewater: 4^4 Orthogonal factorial experiment was also used in the Selection and interaction of factors in the electrochemical treatment method. Table 4.3b presents the results of percentage removal of suspended solids from the wastewater. The result shows that the process is efficient in removing suspended solid from the wastewater as it shows the ability to remove 99.69% of the contaminant after electrochemical treatment. Apparently, Suspended solids are susceptible to removal by electrochemical processes. This further showed that the best combination for the removal of suspended solids is at an operating time of 30 minutes, stirring speed of 170 rev/min, contact area to volume ratio of 0.17 cm^2/cm^3 and a pH of 8.50.

Table 4.3a Results of Percentage Removal of Turbidity from the Wastewater

Experiment	Time (min.)	Ss (Rev/min)	Cv (cm^2/cm^3)	pH	Sample 1	Sample 2	Sample 3	Sample 4	Average
1	1	1	1	1	26.36	22.33	3.05	3.05	13.70
2	1	2	2	2	16.33	20.83	8.72	8.72	13.65
3	1	3	3	3	5.84	5.84	3.31	3.31	4.58
4	1	4	4	4	0.27	20.37	6.39	6.39	8.36
5	2	1	3	2	25.32	22.33	11.64	11.64	17.73
6	2	2	4	1	24.57	23.07	6.39	6.39	15.11
7	2	3	1	4	26.07	6.59	3.05	3.05	9.69
8	2	4	2	3	3.14	4.34	0.00	0.00	1.87
9	3	1	4	3	26.26	22.33	11.64	11.64	17.97
10	3	2	3	4	24.17	19.33	6.39	6.39	14.07
11	3	3	2	1	3.45	11.09	8.72	8.72	7.99
12	3	4	1	2	8.86	0.27	3.05	3.05	3.81
13	4	1	2	4	42.07	40.83	45.88	40.88	42.42
14	4	2	1	3	37.83	36.33	30.72	28.72	33.40
15	4	3	4	2	22.40	26.59	28.39	36.39	28.44
16	4	4	3	1	10.27	33.14	23.05	28.50	23.74

Removal of Total Solid from the Wastewater: Table 4.3c presents the results of percentage removal of total solid from the wastewater. The result shows that the process is efficient in removing suspended solid from the wastewater as it shows the ability to remove 80.72% of the contaminant after electrochemical treatment. The combination of factors that gives the optimum removal stands at an operating time of 30 minutes, stirring speed of 130 rev/min, contact area to volume ratio of 0.33cm^2/cm^3 and a pH of 4.50

Table 4.3c Results of Percentage Removal of Total Solids from the Wastewater

Experiment	Time (min.)	Ss (Rev/min)	Cv (cm^2/cm^3)	pH	Sample 1	Sample 2	Sample 3	Sample 4	Average
1	1	1	1	1	82.33	92.19	81.94	58.33	78.70
2	1	2	2	2	85.94	89.06	79.17	2.78	64.24
3	1	3	3	3	76.56	82.81	23.61	79.17	65.54
4	1	4	4	4	85.94	93.75	12.50	23.61	53.95
5	2	1	3	2	81.25	90.63	87.50	40.28	74.91
6	2	2	4	1	89.06	92.19	70.83	70.83	80.73
7	2	3	1	4	92.19	85.94	40.28	27.78	61.55
8	2	4	2	3	89.06	29.69	23.61	44.44	46.70
9	3	1	4	3	93.75	21.88	86.11	16.67	54.60
10	3	2	3	4	95.31	95.31	65.28	30.56	71.61
11	3	3	2	1	85.94	14.06	27.78	87.50	53.82
12	3	4	1	2	93.75	90.63	2.78	70.83	64.50
13	4	1	2	4	67.19	39.06	79.17	86.11	67.88
14	4	2	1	3	95.31	25.00	58.33	4.17	45.70
15	4	3	4	2	82.81	40.63	12.50	4.17	35.03
16	4	4	3	1	87.50	48.44	1.39	12.50	37.46

Conclusions

Based on the strength of the results, the study has established the following facts in relation to the objectives of the research work:

i. The wastewater from the gold mining sites contained Turbidity, Suspended Solids, Total Solids and pH.

ii. Wastewater from a gold mining site could be subjected to electrochemical treatment method and effectively remove the selected contaminants (Turbidity, Chloride, Suspended Solids and Total Solids).

iii. Aluminum rod can be used as electrode that can be used effectively with minimal dissolution during the electrolysis.

Recommendations

Even though, the research work has dealt extensively with the removal of the physic-chemical contaminants, some grey areas are yet to be worked on for example:

Further studies should be carried out on the wastewater to investigate the types of dissolved heavy metals present and the efficiency of the treatment method in removing them.

Adequate studies on the efficiency of the process to remove the contaminants using other electrodes should be documented to compare the removal rates to that employed in this research work.

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