

Solvent and Concentration Effects on Electrocoagulation of Quinones

V. N. Mkpenie¹, E. A. Essien^{2*}, U. J. Etim³

^{1,2,3}Department of Chemistry, Faculty of Science, University of Uyo, Nigeria

Abstract: *Quinones, 1, 4-benzoquinone and 8-hydroxyquinoline were subjected to electro-coagulation. The rate and extent of coagulation of these compounds appeared to correlate with the presence of phenolic substituent groups and decree of water/ethanol composition in the solvent system. 8-hydroxyquinoline was best electrocoagulated in 75% aqueous ethanol within 30 minutes, while 1, 4-benzoquinone showed a fastest coagulation in 25% aqueous ethanol at 0.01% (w/v) in time less than 50 minutes. Both quinones show electrocoagulation trend of 0.01% > 0.1% > 1.0% in 0.01% (w/v) solvent system. On the whole, 1, 4- benzoquinone showed enhanced coagulation under the study conditions.*

Keywords: Electrocoagulation, 1, 4-benzoquinones, 8-hydroxyquinolines, solvent.

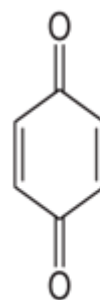
1. Introduction

One of the major challenges facing mankind today is the production of clean water to a vast majority of the population around the world. The need for clean water is particularly critical in the third world countries, river canals, and estuarine and other water bodies are being constantly polluted due to indiscriminate discharge of industrial affluent as well as other anthropogenic activities and natural processes. In the later unknown geochemical processes have contaminated ground water with arsenic, in many highly developed countries, such as the US are also experiencing a critical need for water urbanization and donates changes thus the reuse of wastewater has become an absolute necessity. There is therefore, an urgent need to develop innovative, more effective and in expensive techniques for treatment of wastewater.

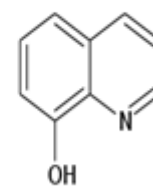
A wide range of waste water treatment techniques are known which includes biological processes for denitrification, phosphorous removal, as well as physiochemical processes that require chemical addition such as adsorption[11][6]. Electrocoagulation is the process of destabilizing suspended, emulsified or dissolved contaminants in aqueous medium by introducing an electrical current into the medium [16]. The electrical current provides electromotive force to drive the chemical reactions. When reactions are driven or forced, the elements or compounds will approach the most stable state. Generally, this state of stability produces a solid that is either less colloidal or less emulsified (or soluble) than the compound at equilibrium values. As this occurs, the contaminants form hydrophobic entities that precipitate and can easily be removed. This method of separation presents considerable advantages over other methods by the addition of chemical such as salts of aluminum and iron are simple equipment and easy operation, a shortened reactive retention period, a reduction or absence of equipment for adding chemicals and a decreased amount to precipitate or sludge [10]. Already, it has been documented as being successful versatile to municipal water treatment [14],[13], dye and textile wastewater treatment [5],[8],[7], oily water treatment [2],defluoridation of water[9]dechlorophyllation[17] and heavy metal removal [12],[1]. Here we find extension of this

technique to the field of plant processing, in the recovery phenolic compounds in plant extracts, which tend to precipitate and denature proteins. Their removal from the extracts is essential, since they have a large impact on the plant downstream performance [16]. In the present work we studied the application of an electric current to coagulate quinones. Quinones are common biologically relevant molecules, one of a class of aromatic quinones in which cations atoms of carbonyl groups are part of the ring structures. 1, 4-benzoquinone or *p*-benzoquinone (Fig.1a) is the basic structure of quinonoid compounds with interesting chemistry.They are an important class of compounds, yellow in colour, which serve as valuable building blocks in synthesis and are key moieties in the synthesis of biologically active compounds[18].

8-Hydroxyquinoline (Fig1b) is derivative of heterocyclequinoline by placement of an OH group on carbon number 8. This light yellow compound is widely used commercially, and at the same time has caused nuisance due to it toxicity potentials. It is generally synthesized in that laboratory by "Skraup" process but in the present study, 8-hydroxyquinone is synthesized from plant. These organic compounds are usually not only costly but also a potential toxic burden to the environment, if treated in the proper way. Therefore isolation and purification of these substances from their natural sources are of paramount importance for their applications in a reasonably pure state. Processing of these compounds by electrocoagulation is preferable due to cost and environmental friendliness of the process.



1, 4-Benzoquinone



8-Hydroxyquinoline

Figure 1: Structures of (a) 1, 4-Benzoquinone and (b) 8-Hydroxyquinoline

2. Materials and Methods

2.1 Synthesis of Quinones

1, 4-benzoquinones was synthesized from phenol according to Teuber reaction [15] which uses Fremy's salt [potassium nitrodisulfonate, $(KSO_3)_2NO$] as oxidizing agent. The 8-hydroxyquinoline used in this study was synthesized from plant, (*Xanthosomamaaffa*). Leaves (500g) of the plant were collected locally, washed with doubly distilled water and sun dried. The leaves were reduced to powder and macerated with 70% ethanol in a conical flask and left for 72 hours, evaporated to dryness in vacuo at 40°C and the dry extract kept in refrigerator prior to use.

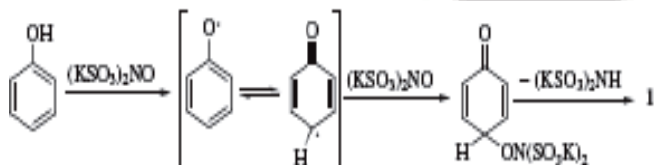


Figure 2: Synthesis of 1, 4-benzoquinone by Teuber reaction

2.2 Preparation of Sample Solutions for Electrocoagulation

The sample solutions (1, 4-benzoquinone and 8-hydroxyquinoline), were prepared in aqueous (25, 50, 75, and 100% (w/v) ethanol solution. In each case 0.01, 0.1 or 1.0g of the quinone salts were added to 10ml of the ethanol solutions and shaken sometimes until properly mixed. The resulting solutions were subjected to electrocoagulation for two hours.

2.3 Electrocoagulation Experiments

Two aluminum plates (dimensions 15 x 4 cm) were used as electrodes. These were spaced 3 cm apart and dipped 6.0 cm deep into a magnetically-stirred aqueous solution (250 ml) of the tested compound (0.01, 0.1 or 1.0% (w/v) solution) in a 400 ml beaker. Sodium chloride (0.5 g) was added as an electrolyte. Direct current (0.9 A, 24-25V) from the DC power supplier was passed through the solution. Every 15 minutes during a 2 hour period of electrolysis, a 3 ml sample of the solution was withdrawn, centrifuged and taken for an absorbance measurement at an appropriate wavelength (380nm and 410nm for 1, 4-benzoquinone and 8-hydroxyquinoline respectively) in a UV-visible spectrophotometer model: Unicam λ 105, Japan. The measured absorbance was then converted into the residual weight percentage of the compound by a calibration curve obtained from a plot of the absorbance versus the concentration for each compound.

3. Results and Discussions

3.1 Solvent Effect on Electrocoagulation of Quinones

The effect of solvent was studied for solvent system consisting of 25, 50, 75, and 100% ethanol. The electrocoagulation of 8-hydroxyquinoline, is fastest in 75% aqueous ethanol, reaching coagulation point in 30 minutes (Figures 1 & 3). Conversely, variation is noted for 0.1%

concentration. For 1, 4-benzoquinone, electrocoagulation is fastest in 0.01% reaching coagulation point in time less than 20 minute (25% ethanol). Coagulation is completed in about 50minutes (0.1%) in same solution of ethanol. For both quinones, the trends of solvent effect are as follows 8-hydroxyquinoline: 0.01% > 0.1% > 1.0% (Figures 1 - 3); 1, 4-benzoquinone: 0.01% > 0.1% > 1.0% (Figures 4 - 6). In figures 2 and 6, enhanced coagulation is recorded in 100% ethanolic extract. From the above presentation, it is seen that decrease in percentage of water in the alcoholic-water systems has some negative tendencies to coagulation. This may be due to only a single mode of coagulation being in operation and more quinones being dissolve as the water content in the solvent system decreases [4].

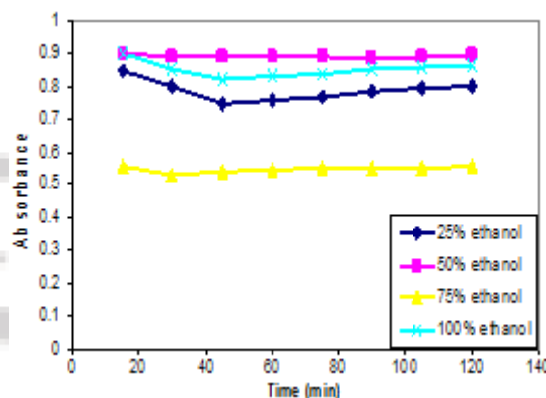


Figure 1: Solvent effect on electrocoagulation of 0.01% (w/v) 8-hydroxyquinoline

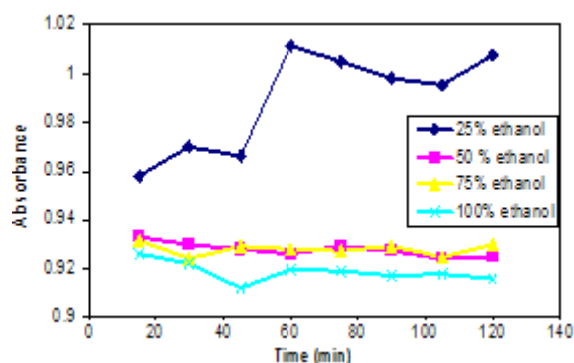


Figure 2: solvent effect on electrocoagulation of 0.1% (w/v) 8-hydroxyquinoline

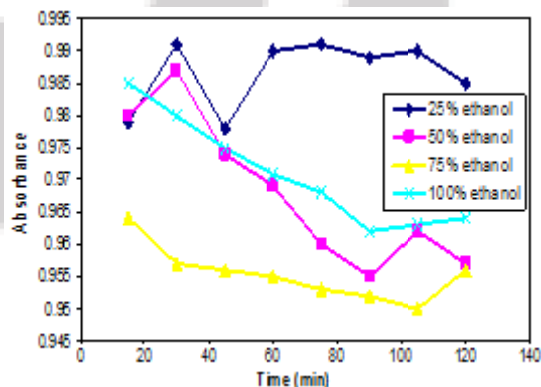


Figure 3: solvent effect on electrocoagulation of 1.0% (w/v) 8-hydroxyquinoline

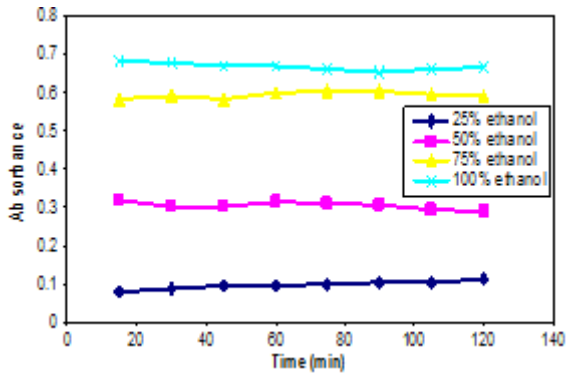


Figure 4: Solvent effect on electrocoagulation of 0.01% (w/v) 1, 4-Benzoquinone

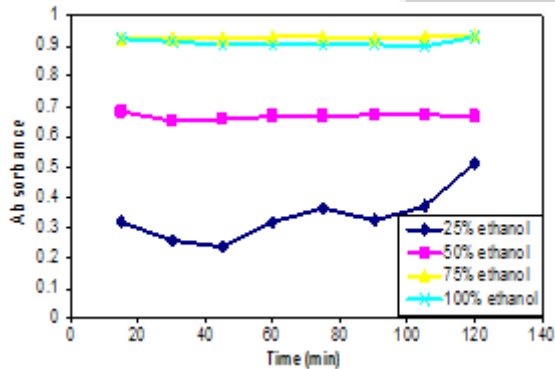


Figure 5: Solvent effect on electrocoagulation of 0.1% (w/v) 1, 4-benzoquinone

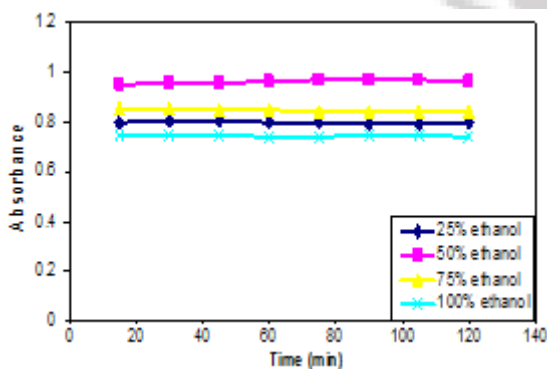


Figure 6: Solvent effect on electrocoagulation of 1.0% (w/v) 1, 4-benzoquinone

These variations may be related to different absorption behaviour and also for different concentrations in the various solvent systems. Generally, the variation in the solvent effects on the electrocoagulation properties of the two organic compounds could be traced to the aromatic substituents, polarity and the solubility in the ethanol solution [14]. The presence of the polar substituents on the aromatic structure induces solubility and thus does not enhance proper electrocoagulation, as compared to a non-polar, non-soluble organic pigment which could be electrocoagulated easily due to immiscibility imposed by the non-polar group.

3.2 Effect of Concentration on Electrocoagulation of Quinone

The effect of concentration was also studied in the electrocoagulation process. In 100% ethanol, 8-hydroxyquinoline and benzoquinone coagulate faster at

0.01% (w/v) concentration at within the first 45 minutes. Highest absorbance is recorded for 8-hydroxyquinoline at 1.0% (w/v) (Figure 7) while 1, 4-benzoquinone has highest absorbance at 0.10% (w/v) concentration (Figure 8). 8-hydroxyquinoline recorded higher absorbance at 1.0% (w/v) then benzoquinone at the same concentration, though electrocoagulation at this concentration was faster for benzoquinone reaching coagulation points within 60 minutes whereas, 8-hydroxyquinoline coagulation within 90 minutes. This disparity may be attributed to the number of OH groups present in the quinones and available for adsorption.

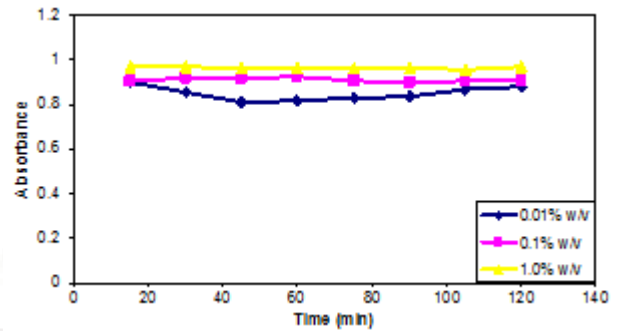


Figure 7: Concentration effect on electrocoagulation of 8-hydroxyquinoline

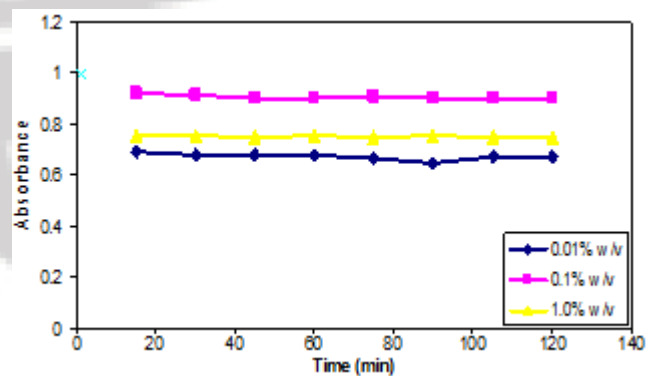


Figure 8: Concentration effect on electrocoagulation of 1, 4-Benzoquinone

Table 1: Electrocoagulation of 0.01% w/v 1, 4-Benzoquinone and 8-hydroxyquinoline in 25% ethanol

Time (min)	Absorbance	
	1, 4-Benzoquinone	8-Hydroxyquinoline
15	0.78	0.991
30	0.782	0.994
45	0.787	0.993
60	0.788	0.996
75	0.789	0.995
90	0.79	0.996
120	0.792	0.995

Table 1 shows the absorbance of the quinones of 0.01% in 25% ethanol solution. For all electrolysis time, 1, 4-benzoquinone coagulates faster than 8-hydroxyquinoline. Both quinones reach maximum in 15 minutes but further retention in the system shows insignificant desorption into the system.

4. Conclusion

Structural composition of substituent groups is a major factor, which often determine the susceptibility or ruler ability to electrocoagulation of organic compounds thus, the

less an organic compound contain or carries a polar group the lesser the time it takes for solvent to affect its electrocoagulation potential. It has also been determined that the presence of hydroxyl-group (a polar group) brings about solubility in alcoholic solution thus, solubility of an organic compound in another increases the time of electrocoagulation. Benzoquinone an organic compound with hydroxyl group, has a higher solvent effect on its electrocoagulation potential, than 8-hydroxyquinoline with one hydroxyl group, has a lower solvent effect on its electrocoagulation potential of solute and vice versa. Electrocoagulation increases as the volume of ethanol in the solvent system decreases.

References

- [1] Balasubramanian, N.&Madhavan, K. Arsenic removal from industrial effluent through electrocoagulation. *Chem. Eng. Technol.* 24: 519–521, 2001.
- [2] Balmer, L. M. &Foulds, A. W.. Separation oil from oil in water emulsions by electroflocculation/ electroflotation. *Filtr. Sep.*, 366–370, 1986
- [3] Chairungsi, N., Jumptong, K., Suebsakwong, P., Sengpracha, W., Phutdhawong, W &Buddhasukh, D. Electrocoagulation of Quinone Pigments, *Molecules*, 11: 514-522, 2006.
- [4] Chairungsi, N., Jumptong, K., Phutdhawong, W. &Buddhasukh, D. Solvent Effects in electrocoagulation of Selected Plant Pigments and Tannin, *Molecules*, 11: 309-317, 2006.
- [5] Do J. S. & Chen, M. L. Decolourization of Dye-Containing Solution by Electroagulation. *J. Appl. electrochem.*, 24: 785-790, 1994.
- [6] Etim, U. J., Umoren, S. A. &Eduok, U. M. Coconut coir dust as a low cost adsorbent for the removal of cation dye from aqueous solution. *Journal of Saudi Chemical Society*, September 2012. <http://dx.doi.org/10.1016/j.jscs.2012.09.014>.
- [7] Gurses, A., Yalcin, M. &Dogar, C. Electrocoagulation of some reactive dyes: a statistical investigation of some electrochemical variables. *Waste Manage.* 22: 491-499, 2002.
- [8] Han, M. & Kwon, A.. Preliminary investigation of electrocoagulation as a substitute for chemical coagulation. *Water Sci. Technol.: Water Supply*, 2: 73–76, 2002.
- [9] Mameri, N., Yeddou, A.R., Lounici, H., Belhocine, D., Grib, H., Bariou, B. Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes. *Water Res.* 32: 1604–1612, 1998
- [10] Lee, B. S., Son, E. J., Choe, E. K. & Kim, J. W. Electrochemical Treatment of Dyeing Effluent Using Sacrificial Iron Electrodes. *J. Korean Fiber Soc.*, 36: 329-337, 1999.
- [11] Lin, S. H. & Wu, C. L. Electrochemical removal of nitrite and ammonia for aquaculture. *Water Res.* 30: 715–721, 1996.
- [12] Osipenko, V. D. &Pogorelyi, P. I. 1977. Electrocoagulation neutralization of chromium containing effluent. *Metallurgist* 21: 44–45.
- [13] Pouet, M. F. & Grasmick, A. Urban wastewater treatment by electrocoagulation and flotation. *Water Sci. Technol.* 31: 275–283, 1995.

- [14] Pouet, M. F. &Persin, F. Intensive treatment by electrocoagulation-flotation tangential flow microfiltration in areas of high seasonal population. *Water Sci. Technol.* 25: 247–253, 1992.
- [15] Teuber, H. J. &Glosauer, O. *Chem. Ber.* 98: 2643, 1965.
- [16] Phutdhawong, W.; Chowwanapoonpohn, S.; Buddhasukh, D. Electrocoagulation and Subsequent Recovery of Phenolic Compounds. *Anal. Sci.* 16:1083-1084, 2000.
- [17] Yılmaz, A. E., Boncukcuoğlu, R., Kocakerim, M. M. A Quantitative Comparison between Electrocoagulation and Chemical Coagulation for Boron Removal from Boron-Containing Solution, *Journal of Hazardous Materials*, 149: 475-481, 2007.
- [18] Vik, EA, Carlson, D. A, Eikun, A. S and Gjessing, ET. Electrocoagulation of potable water, *Water Research*, 18; 11: 1355-1360, 1984.

Author Profile



Essien, Edidiong received his B. Sc (Dec, 2006) and M.Sc (August, 2011) degrees from University of Uyo in Applied Chemistry and Analytical Chemistry respectively. He has been involved in

Analytical/Environmental Researches. He strongly promotes and stimulates chemistry for human development by supporting and participating in researches.



Mkpennie, Victor N. is a practicing inorganic chemist. He received his B.Sc. degree in chemistry in 2000 from University of Uyo, Nigeria and M.Sc. in 2006 from University of Port Harcourt, Nigeria. He has received an award of excellence in academic. His current research includes solution chemistry, synthesis of metal complexes and evaluation of structure- activity relationship and application of the complexes in biological studies.



Etim, U. J. graduated from University of Uyo, Nigeria with B.Sc and M.Sc in Applied Chemistry in 2006 and 2012 respectively. With interest in academics he is currently on his PhD. Etim, is research active and has worked in various researches in absorption polymers.